For Reference

NOT TO BE TAKEN FROM THIS ROOM

For Reference

NOT TO BE TAKEN FROM THIS ROOM

Ex libris
universitatis
albertaensis

University of Alberta
Printing Department

Digitized by the Internet Archive
in 2019 with funding from
University of Alberta Libraries

https://archive.org/details/Rosenfield1960

Thesis
1960(F)
#2D

THE UNIVERSITY OF ALBERTA

AN INTERFEROMETRIC STUDY OF CONCENTRATION POLARIZATION AT LOW CURRENT DENSITIES

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS OF THE DEGREE
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

by

CHRISTINE ANN CULP ROSENFIELD, B.S.(CHEM.)

EDMONTON, ALBERTA

June 10, 1960

ABSTRACT

The electrolysis of cupric sulphate is extensively studied by the use of an interferometric method. A bipartite fringe pattern is found. The first portion has been studied with respect to its variation with temperature and electrode separation, and the lack of appreciable variation with concentration, the thickness of the electrodes, the optical arrangement, and the reflectivity of the glass optical flats has been noted. Mathematical relationships expressing the dependance of the first wave on current density are obtained at several temperatures. The first portion of the interference fringe pattern is found to be the diffusion layer, and cationic diffusion constants obtained.

The second portion of the pattern was observed, and several possible mechanisms for its existence considered. The mechanism previously postulated by Ibl is discarded. The dissociation of ion-pairs is found to provide a satisfactory mechanism, if the possibility be admitted that $SO_4^=$ adions might cause a greater-than-normal extent of pairing in the vicinity of the anode. A pH change mechanism is also found potentially possible.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. R.N. O'Brien for his most valuable advice, direction, and encouragement throughout this work; also, the University of Alberta, for a teaching fellowship during the 1957-58 and 1958-59 academic years; the National Research Council of Canada for a fellowship dufing the summer of 1958; and the International Nickel Company for a teaching fellowship during the 1959-60 academic year.

TABLE OF CONTENTS

PAGE

Abstract....................................i

Acknowledgement............................ii

Table of Contents..........................iii

List of Tables.............................iv

List of Figures.............................v

List of Interferograms.....................vi

Introduction................................1

Instruments and Procedures.................10

Data

Part 1. Reproducibility...................27

Part 2. Limitation of the variables......33

Part 3. Temperature dependance of the first wave........................52

Part 4. The effect of electrode separation..........................67

Part 5. Solutions other than $CuSO_4$.......74

Interpretation:First Wave..................79

Interpretation:Second Wave.................87

Summary...................................109

Bibliography..............................111

Appendix..................................114

LIST OF TABLES

page

Table I. The reproducibility of the first-wave shift at the anode....................28

Table II. The electrodes less than 1.92 millimeters in thickness...........................34

Table III. The variation of the first wave with concentration...................39

Table IV. Reticule measurements of the first wave at the cathode.................44

Table V. The variation of the first wave with the optical reflectivity of the flats....48

Table VI. Reflection Technique.................50

Table VII. The temperature dependance of the first wave in a 10 grams per liter solution of $CuSO_4$..........................53

Table VIII. The dependance of first wave shift on electrode separation...........68

Table IX. Diffusion constants of Cu^{++} in $CuSO_4$ at various temperatures.............85

Table X. Molar refractions and ionic refractions as determined by Luhdemann and Fajans.101

LIST OF FIGURES

page

Figure 1. Diagram of a typical fully-developed interference pattern....................8

Figure IIA. Optical arrangement in the transmission method....................11

Figure IIB. Optical arrangement in the reflection method........................13

Figure III. The cell................................18

Figure IV. The electrical circuit.................24

Figure V. Linear and exponential best-fit lines....29

Figure VA. High and low current density exponential best fit lines showing small electrode separation data..........................31

Figure VI. Concentration dependance, anode........40

Figure VII. Concentration dependance, cathode from interferogram measurements.......41

Figure VIII. Concentration dependance, cathode, from reticule measurements.............45

Figure IX. Temperature dependance, anode...........62
(Temperature contours)

Figure X. Temperature dependance, anode...........63
(Current density contours)

Figure XI. Temperature dependance of threshold current density..........................65

Figure XII. Electrode separation dependance........73

LIST OF INTERFEROGRAMS

page

1. Examples of single- and double-interference-pattern systems..............................20
2. .25 mm. electrodes, 1600 μA/cm^2, 7.5°C., 30 g/l..35
3. 2 mm. electrodes, 1600 μA/cm^2, 7.5°C., 30 g/l ...35
4. 1 g/l, 1600 μA/cm^2, 7.5°C........................42
5. 10 g/l $CuSO_4$, no current, 7.5°C. 55
6. 10 g/l $CuSO_4$, 200 μA/cm^2, 7.5°C...................56
7. 10 g/l $CuSO_4$, 400 μA/cm^2, 7.5°C...................57
8. 10 g/l $CuSO_4$, 600 μA/cm^2, 7.5°C...................58
9. 10 g/l $CuSO_4$, 800 μA/cm^2, 7.5°C...................59
10. 10 g/l $CuSO_4$, 1000 μA/cm^2, 7.5°C..................60
11. 10 g/l $CuSO_4$, 1400 μA/cm^2, 7.5°C..................61
12. Threshold current, 100 μA/cm^2, 6°...............66
13. Threshold current, 300 μA/cm^2, 42°..............66
14. $NiSO_4$-$CuSO_4$ comparison.............................77

CHAPTER 1

INTRODUCTION

The purpose of this work was to extend knowledge of electrode processes at a working copper electrode by the use of an optical method similar to that described by Samarcev[1], and independently developed by O'Brien[2]. The efforts of the previous workers are extended by means of a study of the dependance of the interference pattern previously observed on temperature, and the interpretation has been clarified by a more precise theoretical treatment, and by comparison with another metallic solution. The study has been largely carried out at low current densities, since it is in this region that the pattern is least complex; but some work has been done at current densities in the range studied by O'Brien. A plausible explanation is offered for the more complex pattern observed in this region of current densities.

Concentration polarization was defined by Nernst[3] by the equation:

$$E_p = \frac{RT}{nF} \ln \frac{C}{C_0} \qquad (1,1)$$

---

[1] A.G. Samarcev, Z. Physik. Chem., A168, 45 (1934)

[2] R.N. O'Brien and H.J. Axon, Trans. Inst. Metal Finishing, 34, 41-52 (1957)

[3] W. Nernst, Z. Physik. Chem., 2, 613 (1888)

where E_p is the concentration polarization in volts, R is the gas constant, T the absolute temperature, n the number of electrons transferred in the electrode process per reacting molecule or ion, F the Faraday (96,489.9[4]), C the concentration of the solution in the immediate vicinity of the electrode, and C_o the concentration in the bulk of the solution. This Nernst concentration polarization has long been experimentally known to be of the order of millivolts.

The first direct method for the measurement of concentration differences at an electrode was developed by Haring[5]. He wished to ascertain whether any change in pH occurred in nickel plating baths. In his method, the cathode is removed suddenly while electrolysis is in progress, and the adhering solution is squeezed into a beaker and analyzed. This method was used by Brenner[6] for determining the concentration change in a $CuSO_4$ bath. Both workers studied the region about the cathode only.

Brenner also developed another experimental method, called the "freezing" method. In that method, a hollow

---

[4] D.N. Craig and W.J. Hamer, J. Chem. Ed., 37, 5, (1960)

[5] H.E. Haring, unpublished results reported by M.R. Thompson, Trans. Electrochem. Soc., 41, 351 (1922)

[6] A. Brenner, Proc. of the 29th Annual Convention of the American Electroplater's Society, (1941), p. 28

electrode is used, into which partially frozen isopentane is poured a few seconds after the current is turned off. Several seconds later, the electrode and a layer of adhering ice about one millimeter in thickness are removed from the solution. The isopentane is removed from the electrode, and a packing of solid carbon dioxide substituted. Then samples of the thoroughly frozen solution are turned off on a lathe.

The two methods of investigation give results differing from one another by about 10% to 20%. Brenner found that the concentration of metallic ions in solution in the immediate vicinity of the electrode (at a distance less than or equal to .2 millimeter) is reduced to as little as one-half of the concentration of the electrolyte as a whole.

The first means of interferometrically observing the concentration polarization of a solution was developed by Samarcev[7] in 1933. He observed the layer which he interpreted as the diffusion layer, extending as an exponential-shaped concentration gradient about .15 to .20 millimeter (increasing distance with increasing current density) into the $CuSO_4$ solution, and used the data which he obtained to calculate the Nernst concentration polarization

---

[7] A.G. Samarcev, Trudy Gosudarst. Opt. Inst., Leningrad, volume 19, no. 87, pp. 16-25 (1933)

and a number of diffusion coefficients, on a basis of Fick's law of diffusion[8]. However, Samarcev's calculation of diffusion constants is here not considered entirely valid, as Fick's law does not allow for the effect of the applied potential upon the ions. A more refined calculation will be developed here[9]. But Samarcev's work did show that a calculation of diffusion constants on a basis of this optical method gives a greater degree of reproducibility than obtained by other methods. (Samarcev made calculations for $CuSO_4$ at 2 N and .2 N, using data from several photographs at different current dnesities for each of the calculated diffusion constants.)

Ibl[10] studied $CuSO_4$ using a Jamin type interferometer. He noticed, in addition to the diffusion layer seen by Samarcev, what he called an "anomalous maximum" at the cathode and "anomalous minimum" at the anode in what he considered to be concentration. Ibl interpreted this as a convection effect, postulating that it somehow resulted from a diffusion of the anodic diffusion layer to the region of the cathode, and of the diffusion layer near the cathode over to the anode side. Ibl supported this theory

---

[8] A. Fick, Pogg. Ann., 94, 59 (1885)

[9] Chapter Iv, page 79ff.

[10] N. Ibl and R. Müller, Z. Elektrochem., 59, 671-6 (1955)

by placing a diaphragm between the two electrodes. The solution on the anode side of the diaphragm attained a stable concentration greater than that part of the solution on the cathode side. The "anomalous maximum" on the cathode side was not as great as the bulk concentration on the opposite side of the diaphragm, and the "anomalous minimum" on the anode side was greater than the bulk concentration on the cathode side of the diaphragm.

In a later paper[11] Ibl developed an equation for relating the amount of convection to the height of the cell and to the current density:

$$u_m = \left(\frac{(\lambda - 1)\eta\,\omega}{\phi^2\,\lambda^2(\omega + 1)^2} \right)^{1/5} \left(\frac{g\,\alpha\,I\,n_A}{z\,F\,\nu} \right)^{2/5} D^{1/5} x^{3/5} \qquad (1,2)$$

in which u_m is the maximum convective flow velocity, λ, ω, ϕ and η are "parameters influencing the shape of the concentration distribution", I is the current density, α the "densification coefficient" (reciprocal density, in cm^3/mole), x is the "distance from lower end of cathode (coordinate in the vertical direction)", z the valence of the cation, n_A the transference number of the anion, F the Faraday, D the diffusion coefficient (presumably of the salt as a whole) g the gravitational acceleration constant, ν the kinematic viscosity. Thus, the amount of convection should be

---

[11] N. Ibl and R. Müller, J. Electrochem. Soc., 105, 346-53 (1958)

proportional to the 2/5th power of the current density and to the 3/5th power of the height of the cell.

Ibl also calculated the distance from the electrode to the point of maximum convective velocity:

$$\tau = \left(\frac{(\omega + 1)\,\omega^2\,\lambda}{\phi\,\eta^3} \right)^{1/5} \left(\frac{zF\,\nu\,D^2}{g\,\alpha\,I\,n_A} \right)^{1/5} x^{1/5} \qquad (1,3)$$

In Ibl's experiments, collophonium was added to solutions of copper sulphate, and photographs taken of the paths of the particles as they moved in the flow of the solution. His calculated and observed values agreed to two significant figures. This work will be discussed further.

O'Brien[12] has observed the same fringe pattern at current densities primarily between 10 and 40 milliamperes per square centimeter, in solutions of plain $CuSO_4$, sulphate-rich $CuSO_4$, solutions chelated with glycine, ethylenediamine tetra-acetic acid, or propylene diamine. His measurements dealt primarily with the region which he called the "second wave" (the "anomalous maximum and minimum" of Ibl)—an increase in the refractive index of the solution in the region adjoining the diffusion layer at the cathode, and a similar minimum near the anode. At

---

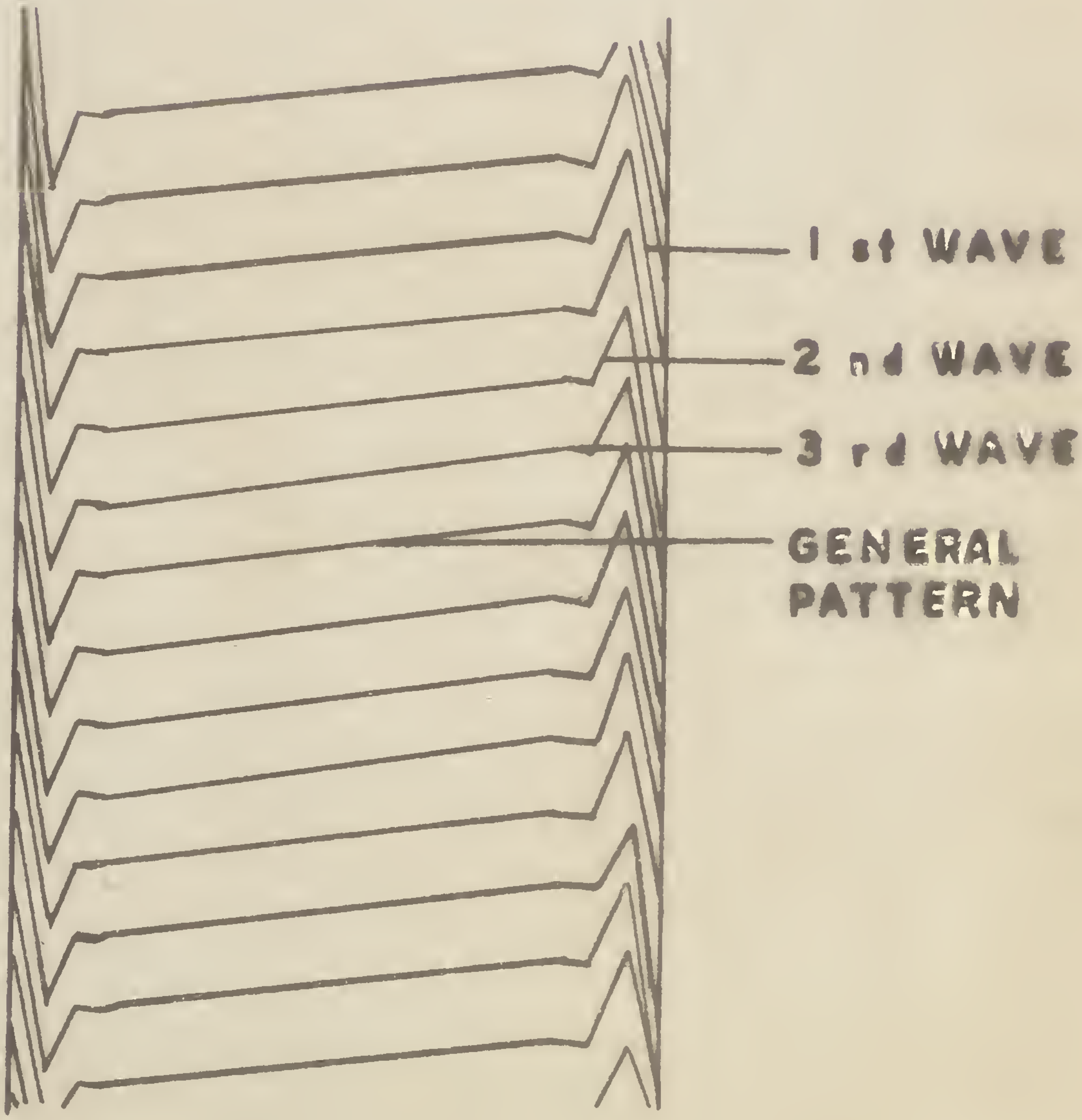
[12] R.N. O'Brien, thesis, "An Optical Study of Electrodeposition", University of Manchester, 1955.

these high current densities, the first wave (the diffusion layer measured by Samarcev) could not be accurately measured, as the many closely-spaced interference fringes could not be resolved.

The nomenclature which O'Brien gave to the pattern of interference fringes will be used henceforth in this work. The "first wave" is the portion of the pattern immediately adjacent to the electrode. This concentration gradient is by far the largest one, sometimes amounting to several grams per liter, or even to the total concentration of the solution. It is the diffusion layer, as Samarcev recognized, and as will be further demonstrated in this work. The "second wave" is the portion of the pattern adjacent to the first wave, and represents a refractive index shift in the direction opposite to that of the first wave. The "third wave" is thought to be a concentration shift yet further from the electrode than the second wave, and in the same direction as the first. It is visible only when the first and second waves have both become quite highly developed, and consequently was not observed in any of the present work. Accepting Samarcev's observation that as current density is increased, the first wave extends progressively further backward from the electrode, the third wave may well be a backward extension of the first. The "general pattern" is the linear portion of the pattern in the bulk

FIGURE I

Diagram of a typical fully-developed interference pattern


1st WAVE
2nd WAVE
3rd WAVE
GENERAL PATTERN

of the solution, between the "waves" at the cathode and anode.

In this investigation, it was intended that a more systematic study of the concentration polarization pattern be made, particularly in $CuSO_4$ solution; and, if possible, that the pattern be explained. This study has been made by determining which variables are important in work of this kind, studying the effects of the important ones, and finally, by comparison with other solutions. It is hoped that this work and the interpretation given to it will help to elucidate the nature of the process of electrodeposition.

CHAPTER II

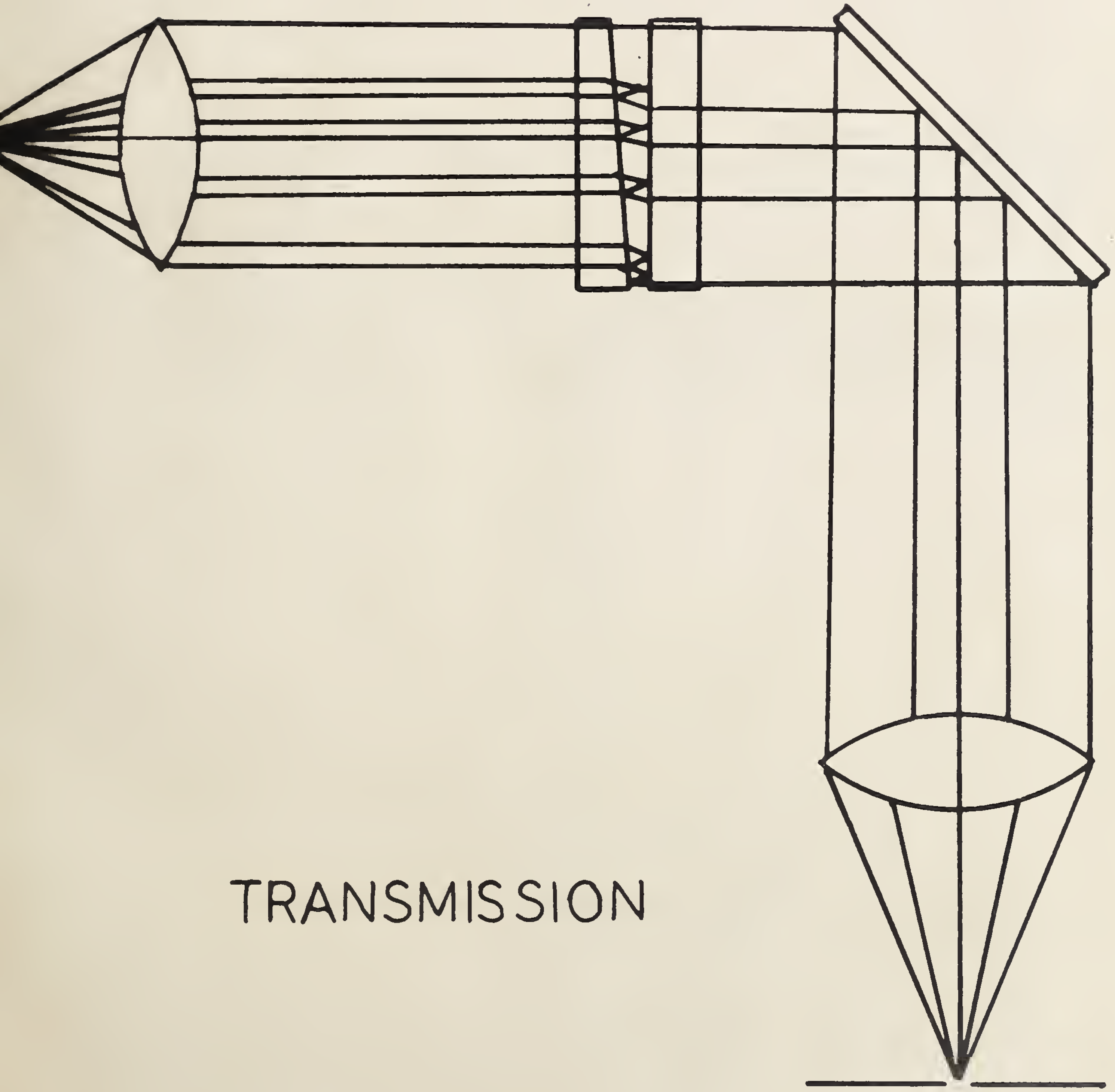
INSTRUMENTS AND PROCEDURES

The principal piece of apparatus used in this investigation was an interferometer arranged in the following manner: A beam of light from a commercial sodium vapor lamp was directed horizontally through a pinhole 1/8" in diameter, in a black mask placed over the opening in the commercial shield. The beam next passed through a double convex collimating lens, placed on the optical axis of the system, from which it emerges as a parallel beam.

Two arrangements were possible at this point: the beam might be directed vertically upward as shown in Figure 1A, by means of a fully-silvered, first-surface mirror placed at a 45° angle to the direction of the beam, and enter the cell above; this is called the transmission method. Or, alternatively, the beam might be directed downward by means of a first-surface, half-silvered mirror, and enter the cell above, as shown in Figure IB; this is called the reflection method. Both methods were found to give the same results, but the reflection method required much longer exposure times, since much of the light was lost to the system, and even so, produced less satisfactory photographs, as perfect adjustment was much more difficult, and in fact, was never achieved with this method.

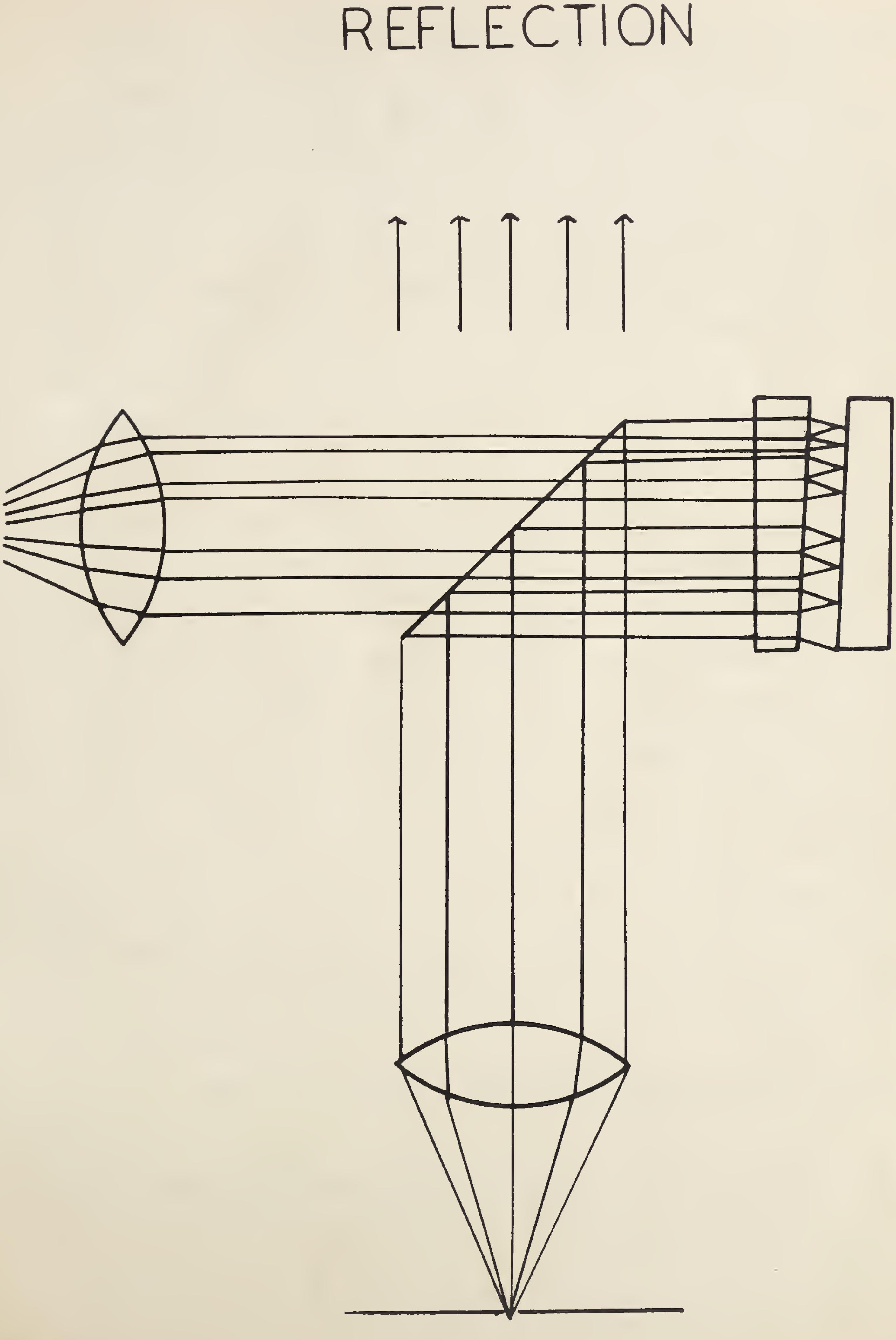
FIGURE IIA

Optical arrangement in the transmission method



TRANSMISSION

FIGURE IIB
Optical arrangement in the reflection method


REFLECTION

The cell itself was cast from Araldite*, and contained a copper coil for circulating coolant to keep the cell at a desired temperature. A reservoir of about 15 liters of water was kept at a temperature controlled to within ± .02° centigrade by a Frigidaire unit. Water from this reservoir was circulated through Tygon tubing by means of a pump. While the temperature in the reservoir itself did not change by more than ± .02° during a run (as determined by a Beckmann thermometer) at some of the higher temperatures the rate at which the water was circulated by the pump was sufficiently slow that the hot water would cool up to 1°C. in the course of flowing through the tubing and cell. The rate of circulation was never changed, and was continued for one half hour to two hours before a run was begun, so that thermal equilibrium was attained. The equilibrium temperature at temperatures more than 10° C. from room temperature differed from the temperature of the solution within the cell, and a correction factor was determined by placing a thermocouple within the cell. The sensitiviy of the thermocouple was about ± .2°C., so the temperatures should be accurate to this extent. Temperatures attained proved to be constant and reproducible.

The cell contained two glass flats, two electrodes,

---

* an epoxy resin manufactured by Ciba

two spacers, and the solution to be studied.

The glass optical flats were first-surface mirrors, coated with the Hi-Efficiency coatings by the Liberty Mirror Division of the Libbey-Owens-Ford Glass Company, of Brackenridge, Pa. It was found that the flats reflecting the most light (coating 901) produced the most distinct systems of interference fringes, as would be expected, since this arrangement produces the largest number of interferring beams[1]. Flats with less reflective coatings (401, 601, 701) transmitted a larger fraction of the incident light, which allowed more light to reach the camera, and consequently permitted shorter time exposures. In this investigation, glass optical flats with reflectivities varying between 40% and 90% (the coatings mentioned above) were used. The non-reflecting faces were at a 1° angle to one another; the coated surfaces were flat, accurate to 1/4 wavelength of the Na_D line.

A series of experiments was performed to determine whether the reflectivity of the flats had any effect on the values obtained. It was found that there is no such effect, as would be expected from the theory involved.

The electrodes used in most of this work were machined from fully-annealled copper, semi-circular in shape, and with

---

[1] S. Tolansky, "Multiple Beam Interferometry", Oxford University Press, (1948), p. 14-18.

a very slight wedge angle (about 0°17') between their horizontal planar faces. A slot was cut in the back of each electrode, into which a piece of sheet copper was inserted, giving the external electrical connection. The pair most used was 1.92 millimeters in thickness, as measured by a vernier caliper. They were 1 1/2" in their greatest dimension, with the 1/4" on each end containing a slight wedge angle into which a Lucite spacer was inserted before a run was begun. The spacers kept the electrodes firmly in place, and prevented current from passing between these portions of the electrode surface.

Thicker electrodes than the 1.92 millimeter ones were found to produce fringe patterns much less distinct in nature, particularly with flats of higher reflectivity. This effect was probably due partly to the fact that the sodium vapor lamp is not absolutely monochromatic, and partly to the wedge angle between the faces of the glass optical flats. These factors tend to disperse the interference fringe into a fuzzy, ill-defined blob of light. The greater degree of absorption of the light by the thicker solution tended to give even less contrast between light and dark fringes. A further complication arises at the cathode, as the decrease in refractive index at the cathode causes the beams to be refracted so as to become superimposed and not capable of being resolved. This is

explained further in Chapter III.

The beam of parallel light, passing into the cell, is divided in amplitude by the optical flats, in either the manner shown in Figure IIA or that in Figure IIB. The optical path length travelled by beams not absorbed or otherwise lost to the system differ from one another by 2aN, where a is the optical path distance through the solution, and N may be any positive integer. The number of reflections does not become larger than about five, due to the light lost in each reflection; it may be as small as about three, depending on the reflectivity of the optical flats used. Two beams only arising from each ray are shown in Figures IIA and IIB for the sake of neatness, but in practice there were three to five. The tiny wedge angle contained in the electrodes themselves caused interference between successively reflected beams, producing a system of interference fringes. Any change in the refractive index of the medium between the electrodes in the direction parallel to the fringe will result in a displacement of the fringe; any change in the direction perpendicular to the fringe would cause an alteration in the spacing of the fringes. For example, an increase in the refractive index will displace the contour of constant optical path length (an interference fringe) toward the vertex of the angle between the two electrode faces; in

this manner, any changes in the refractive index of the solution during electrodeposition may be measured. This is the basis of this investigation.

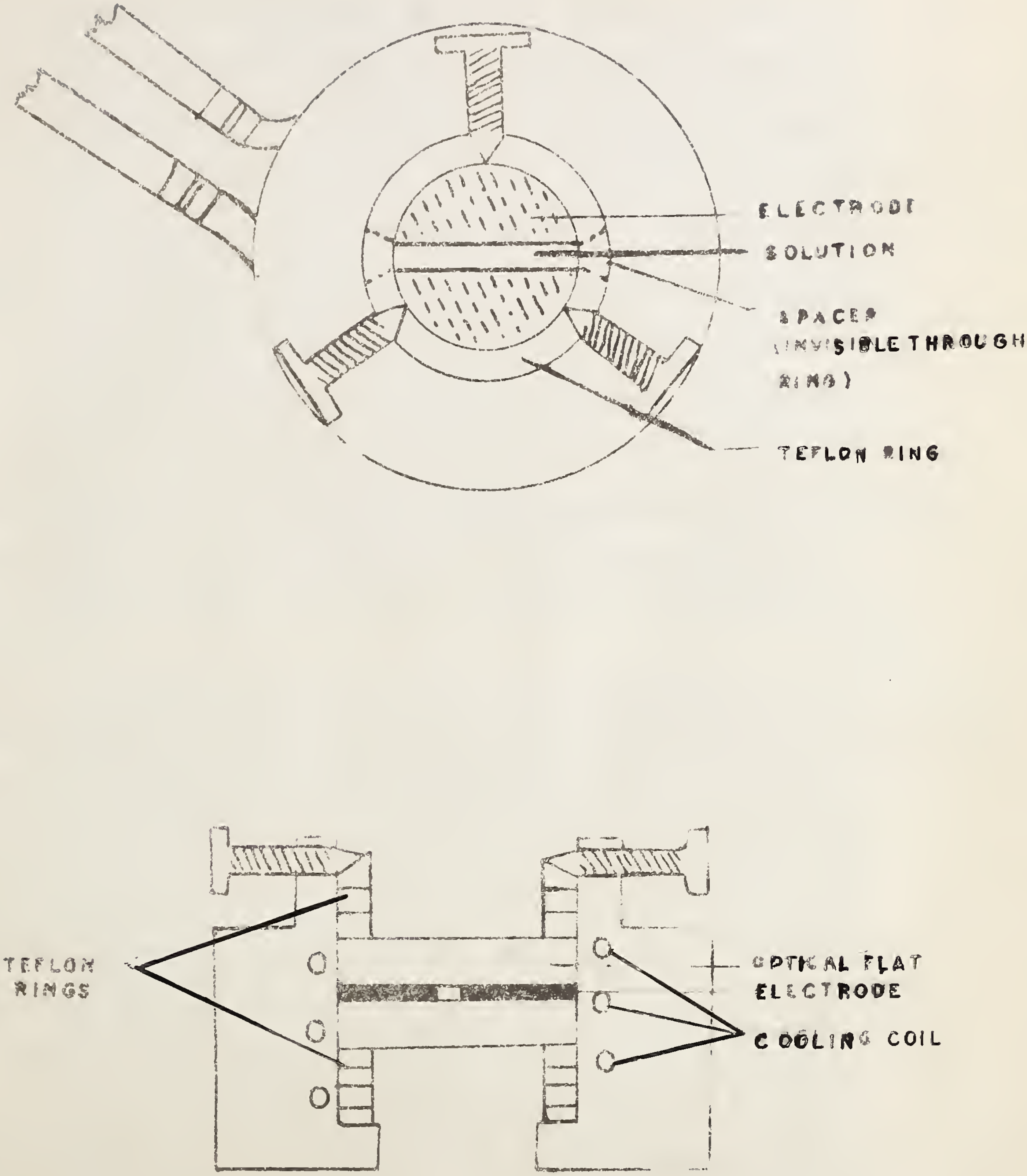
The exact angle between the mirror surfaces of the optical flats could be regulated to a small extent by means of pressure exerted upon three Teflon screws in the side of the cell; the clarity of the fringes could be adjusted by placing bits of plasticene beneath the cell, altering the angle of the incident light by a few minutes of arc to give exactly perpendicular incidence.

Figure II is a scale diagram of the cell.

The several beams emerging from the cell next pass into the microscope, which was an Ernst-Leitz-GMBH-Wetzlar model, with the Leica camera attachment "Makam". This attachment was used with a microscope objective of 50 millimeters focal length and a six power ocular. The film used was Kodak Royal-X panchromatic, in 4" x 5" sheets. These sheets did not quite fit the film holder, and were therefore trimmed before exposure. The film was then placed in the film holder, inserted in the camera, and exposed. Exposures ranged between two and ten minutes, depending on the concentration of the solution, the thickness of the electrodes, the reflectivity of the flats, and on whether the "transmission" or "reflection" method was being used.

FIGURE III

The cell


ELECTRODE
SOLUTION
SPACER (INVISIBLE THROUGH RING)
TEFLON RING
TEFLON RINGS
OPTICAL FLAT ELECTRODE
COOLING COIL

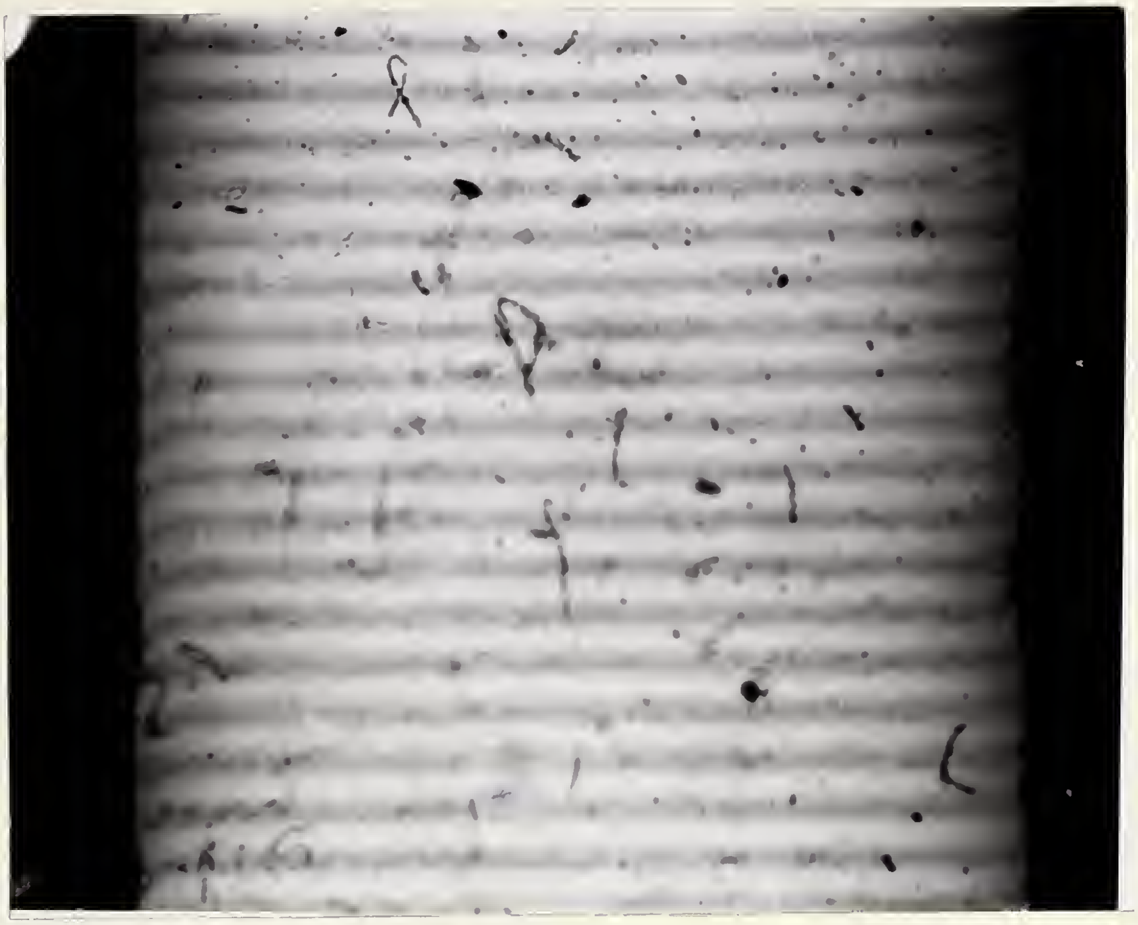
After exposure, the films were stored in a light-tight developing tank until a run was completed. They were then developed for four minutes in total darkness with Kodak D-82 developer, prepared from its constituents according to the formula[2]. They were then treated with an acetic acid stop solution (18 milliliters of glacial acetic acid to 1 liter of solution) for a few seconds, fixed in Kodak Acid Fixer with Hardener for 10 minutes, and washed in running water for about 1 hour. The films were then dried, and printed on F-5 Kodabromide paper. The prints were developed in Kodak Dektol, fixed, washed, and dried in a roll of blotting paper. When dried, they were measured by means of a square millimeter graticule inscribed on a sheet of Lucite.

Insofar as possible, a large number of prints (3 or 4 runs) were measured at one time, to insure a uniform measuring technique. All temperature dependance, reflectivity dependance, and runs with electrodes other than 1.92 millimeters in thickness, for example, were measured at one time, as units. In making the measurements, the photographs were taken from the drying blotter, on which they had been placed at random, and measured as they came, in random order. Shifts were measured, when possible, by the use of the dark line between two light ones (see page 20), as this is the most precisely defined point on the fringes. When no such line existed, the fringes were

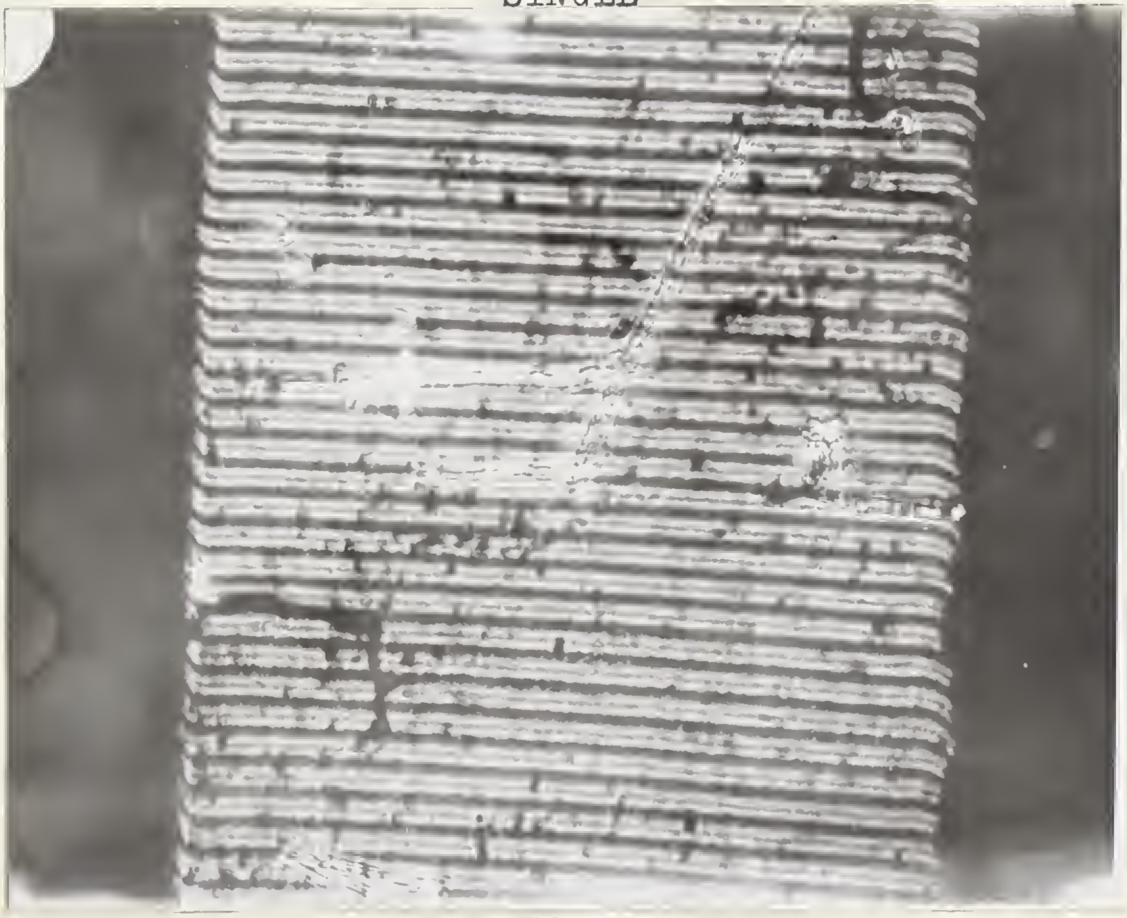
---

[2] Handbook of Chemistry and Physics, 36th Ed., p. 3021, (1955)

EXAMPLES OF SINGLE- AND DOUBLE-INTERFERENCE-FRINGE SYSTEMS


CATHODE
ANODE

SINGLE



DOUBLE

measured from center of one interference fringe to the center of the next. This is a more accurate measurement than either from top-to-top or bottom-to-bottom, since when the shift is large, a fringe is considerably narrower near the electrode than in the main body of the solution, and this consideration should offset the slight loss in precision over measuring from the more precisely defined edge of the interference fringe. The spacing between interference fringes was always measured over several fringes and the average spacing obtained.

When the electrode exhibited a considerable variation in activity from one spot to another, the largest fringe shift was measured, because it was found that this gave the most reproducible result.

When a maximum, or second wave, was present, the measurement was made by extending the general pattern until it again intersected the fringe, and measuring the distance from this point to the furthest extent of the first wave shift.

For these low current densities, it was not critical whether the shift was measured with the grid parallel to the electrode or parallel to the general pattern. Normally the grid was arranged parallel to the general pattern, but some exceptions were made when the photograph was dark and the alternate arrangement facilitated measurement.

Measurements of the general pattern shift were at

first attempted, then later abandoned when it was noted that, where they were of any considerable magnitude, the shifts frequently remained after the current had been turned off. The general pattern shifts are therefore considered to be due to a distortion of the flat under pressure, particularly since they were large most frequently when the adjustment of the fringes required a considerable pressure on the flat from the Teflon screws.

In experiments at higher current densities, a real and very measurable general pattern shift would be noted, and the measurement of this shift would be very useful in measuring the amount of bulk diffusion taking place, and possibly in calculating the relative electrode efficiencies as described by O'Brien[3]. However, in this work, the general pattern shifts did not exceed .1 fringe except when pressure was exerted as already discussed; in this case the general pattern shift depended on time, rather than current density, and will not be considered further.

All solutions except the saturated one were prepared by dissolving a weighed quantity of Baker analyzed reagent anhydrous $CuSO_4$ in distilled water, and filtering the solution through a Gooch crucible. The filtration through a Gooch crucible was conducted in order to remove the inevitable dust and bits of insoluble impurities found even

---

[3] R.N. O'Brien, thesis, op. cit., (1955)

in reagent-grade chemicals. The solutions were not analyzed, since no impurities would be expected in sufficient quantity to affect the pattern being studied. The saturated solution was prepared by dissolving reagent grade $CuSO_4 \cdot 5H_2O$ in hot distilled water, and permitting the excess solute to crystallize out of solution by cooling to room temperature with stirring. A portion of this solution was cooled to 10° C. in the constant-temperature bath. It was first attempted to use this solution without filtration, but the large number of tiny crystals that precipitated out during the run made this impractical. The solution was filtered through a Gooch crucible, removing the microscopic suspended crystals.

Since $CuSO_4$ decomposes on long standing exposed to light,[4] the solutions were kept in the darkroom and not exposed to more light than necessary.

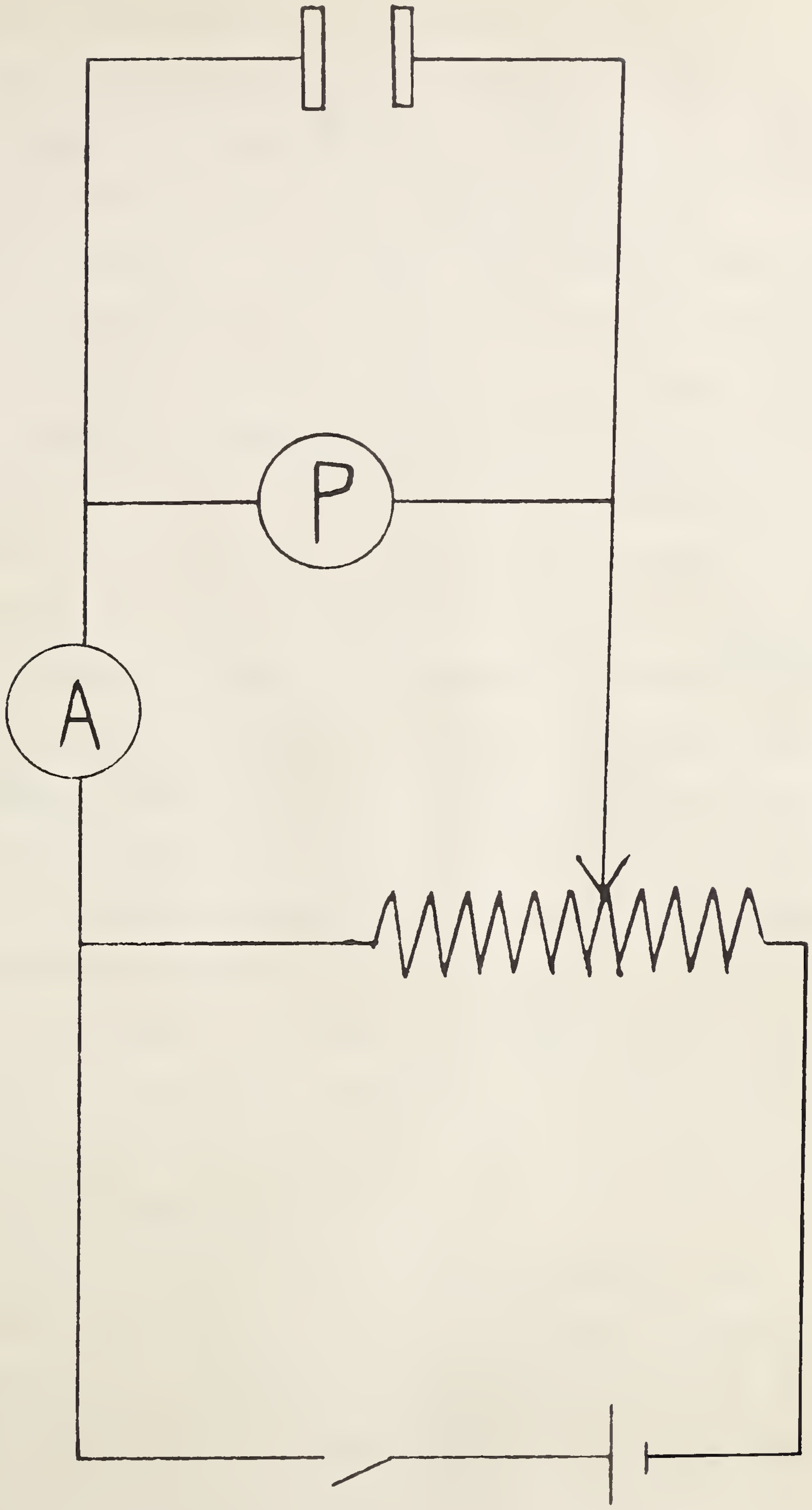
The electrical circuit is shown in Figure III. The galvanometer used with the potentiometer is the G.M. Laboratories Galvanometer, identified as catalogue number 570-401 by a metal plate on the instrument. The potentiometer (P) is the Leeds and Northrup type K. The ammeter (A) is a Simpson D.C. Microammeter, model 284, which has scales giving full-scale deflection at 50, 100, 250, and 1000 microamperes. The standard cell is a product of the

---

[3] M.R. Chakrabarty, this laboratory, unpublished results

FIGURE IV

Electrical circuit



Eppley Laboratory, having a certified potential of 1.01920 volts. The working battery is a lead-storage cell with a 2.2-volt potential, capable of 60 ampere-hours output. It was recharged from time to time during the work.

At the beginning of each run, the desired lower flat was secured in its position by pouring molten paraffin into the bottom of the cell, then putting the flat into position while the paraffin was still very soft. A seal was thus effected, preventing the cell from leaking. The electrodes were then placed in position, secured by two small sector-shaped perspex spacers, the solution poured in, the top flat placed in position, Teflon rings added, and excess solution removed by means of a hypodermic needle. The water was then circulated until the cell reached thermal equilibrium. This point was determined by measuring the temperature of the water flowing out of the cell; when any difference between the temperature of the water flowing into the cell and that flowing out no longer decreased with time, thermal equilibrium was considered to have been obtained. The exact temperature attained for each water temperature used was determined by placing a thermocouple in the cell.

When thermal equilibrium had been obtained, the interference fringes were adjusted as closely perpendicular to the electrodes as could be determined by eye by means of three Teflon screws, and by adjusting the cell's tilt with

plasticene. The camera was loaded, a "no-current" photograph taken; then electrodeposition was begun by fastening the leads from the electrical circuit (Figure III) to the electrodes, and the current turned on by closing the knife switch. All desired additional photographs were taken, in order of increasing current density, and the readings of current and voltage recorded.

On closing the switch in the circuit a steady current was shown on the ammeter. The voltage did not vary, although the stable fringe pattern was not completely developed until about one minute had elapsed. The transient currents found by Bockris[4] are of the order of 10^{-3} seconds in duration, and the present apparatus would not detect such short-lived effects.

At the end of the run, the cell was taken apart, and the glass optical flats and electrodes thoroughly washed with detergent.

---

[4] J. O'M. Bockris and W. Mehl, Can. J. Chem., 37, 199 (1959)

CHAPTER III

DATA

PART 1. Reproducibility

In order to determine the degree of reproducibility inherent in the experimental measurements to be conducted, two runs were performed under conditions as similar as possible. The reservoir was set at a temperature of 4.0°C., and 1.92 millimeter electrodes were used, spaced 3.0 millimeters apart. Photographs were taken at the current densities as shown in Table 1, and the first wave shifts in the interference fringes shown there are plotted in Figure V.

The first wave is interpreted as a change in the concentration of the solution. The interference fringes are contours of constant optical path length; since the flats incorporate a wedge angle, a change in refractive index will deflect the interference fringe. The method for obtaining the exact concentration change will be shown in detail in Chapter IV[1].

The data were fitted first to a linear least-squares relationship; when this was found to give a fit with a probable error larger than expected, a second solution in exponential form was tried. The points at lower

---

[1] Chapter IV, page 73

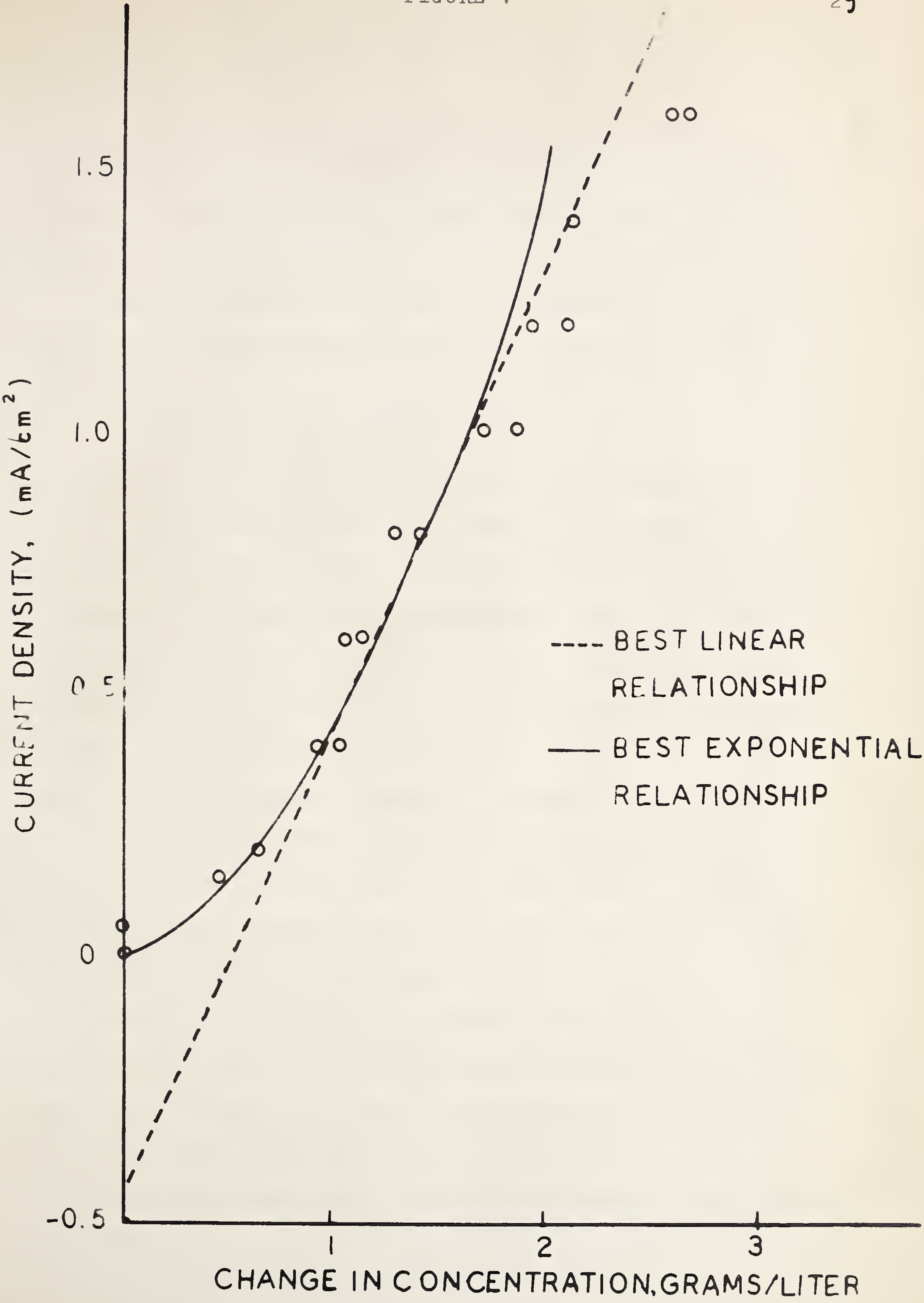
TABLE I

The reproducibility of the first-wave shift at the anode.

Current density $\mu A/cm^2$	Anode shift λ_{Na_D}	Anode shift grams/liter
60	0	0
160	.40	.45
200	.57	.64
400 (a)	.84	.94
400 (b)	.90	1.01
600 (a)	1.00	1.12
600 (b)	.92	1.03
800 (a)	1.12	1.25
800 (b)	1.22	1.37
1000 (a)	1.51	1.69
1000 (b)	1.65	1.85
1200 (a)	1.70	1.90
1200 (b)	1.85	2.07
1400 (a)	1.88	2.11
1400 (b)	1.87	2.10
1600 (a)	2.32	2.60
1600 (b)	2.37	2.66
2000 (b)	2.50	2.80
4000 (b)	4.00	4.48

EFFECT OF FIRST WAVE ON CURRENT DENSITY_ REPRODUCIBILITY

FIGURE V



current densities fit this relationship satisfactorily, but the points at higher current densities do not. Therefore, a third exponential solution was calculated on a basis of these points at higher current densities. The result of this calculation is shown in Figure VA.

Figure V shows the linear and exponential (low current densities) fits. The linear solution is the equation

$$C = 89\,G - 440 \quad (3,1)$$

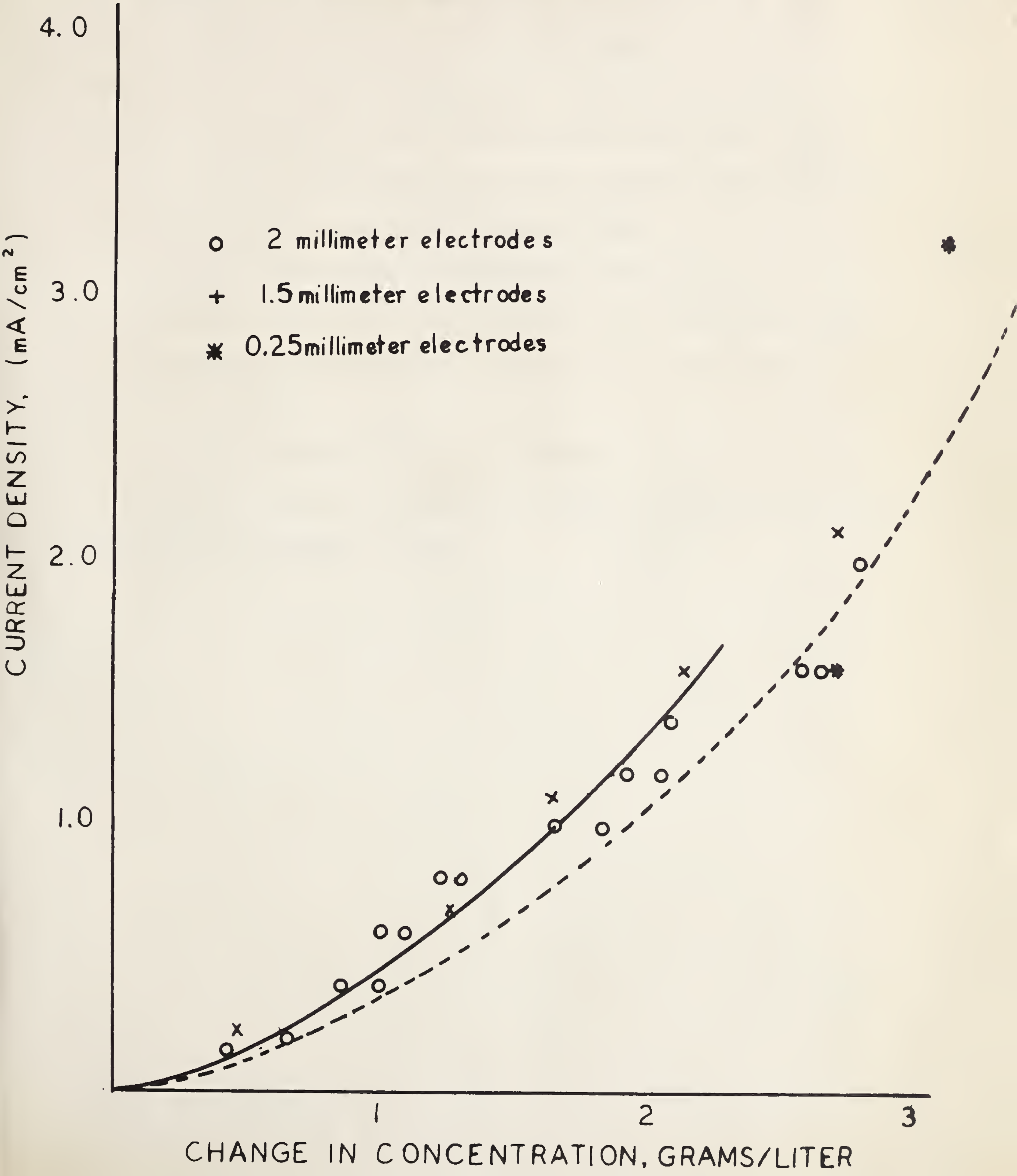
in which C is the current density in microamperes/cm^2 and G is the shift of the first wave at the anode in grams/liter. (The method of arriving at this figure is shown in Chapter IV.) The standard deviation of the experimental points from this solution is ± .224G. This implies an error of nearly 1 millimeter in the measurement of the interferograms, and also implies a fringe shift of .4 grams/liter when no current is passing.

However, no fringe shift has ever been observed when no current is passing. It is difficult to imagine a concentration gradient with no force operating to cause it. The calculated error again implies an error of ± 1 millimeter in measuring the interferograms, which seems unreasonable since the measuring graticule had 1 millimeter square divisions, and it was not considered difficult to visually divide the squares into fifth parts.

The exponential solution by the method of least squares

FIGURE VA

THE EFFECT OF DEPTH OF SOLUTION ON FIRST WAVE SHIFT



for the first thirteen points gives the equation

$$C = 467\ G^{1.62} \qquad (3,2)$$

for current densities of 1200 microamperes/cm^2 and less, with a standard deviation of ± .053G; this implies a probable error about .2 millimeter in the measurement of the interferograms. This is considered the proper degree of experimental uncertainty, so this equation (3,2) should adequately express the relationship found.

A third least-squares solution, performed on the points at the higher current densities (1400 microamperes/cm^2 to 4000 microamperes/cm^2) was found to yield the equation

$$C = 367\ G^{1.65} \qquad (3,3)$$

The solid line on Figure IVA shows equation (3,2); the dotted line, equation (3,3).

Part 2. Limitation of the variables

Since so little previous work has been done using the experimental techniques of this investigation, it is felt desirable to conduct some preliminary investigation of variables which should not, but possibly might have affected the results.

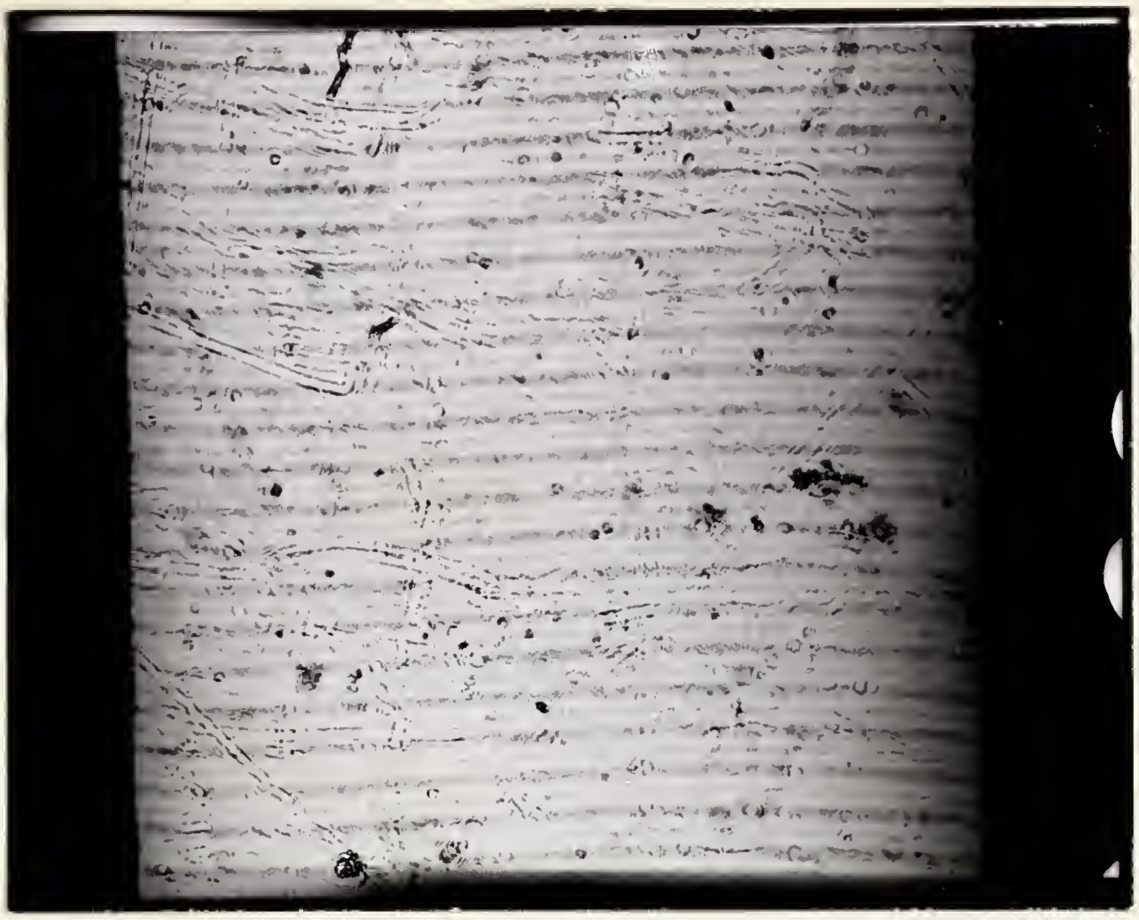
The first such study was an investigation of the possibility that the fringe pattern might be a surface effect arising from the very small volume of solution (about .15 milliliter) being studied, or that the fringe pattern might be a convection effect. In either case, it would depend on the thickness of the electrodes. To test this possibility, runs were conducted using coolant at a uniform temperature of 4.0°C. The temperature of the solution within the cell was 7.5°C. A $CuSO_4$ solution was used which contained 30 grams of anhydrous $CuSO_4$ per liter of solution, and the electrodes were maintained at a constant separation of 3.0 millimeters. Electrodes of thicknesses .25 millimeter, 1.5 millimeter, 1.92 millimeters, 4.0 millimeters, and 10.0 millimeters were used. The results obtained are shown in Tables 1 and 2, and sample photographs are given on page 35. No figures were recorded for the 4.0 millimeter or 10.0 millimeter electrodes, as the fringe pattern obtained with

TABLE II

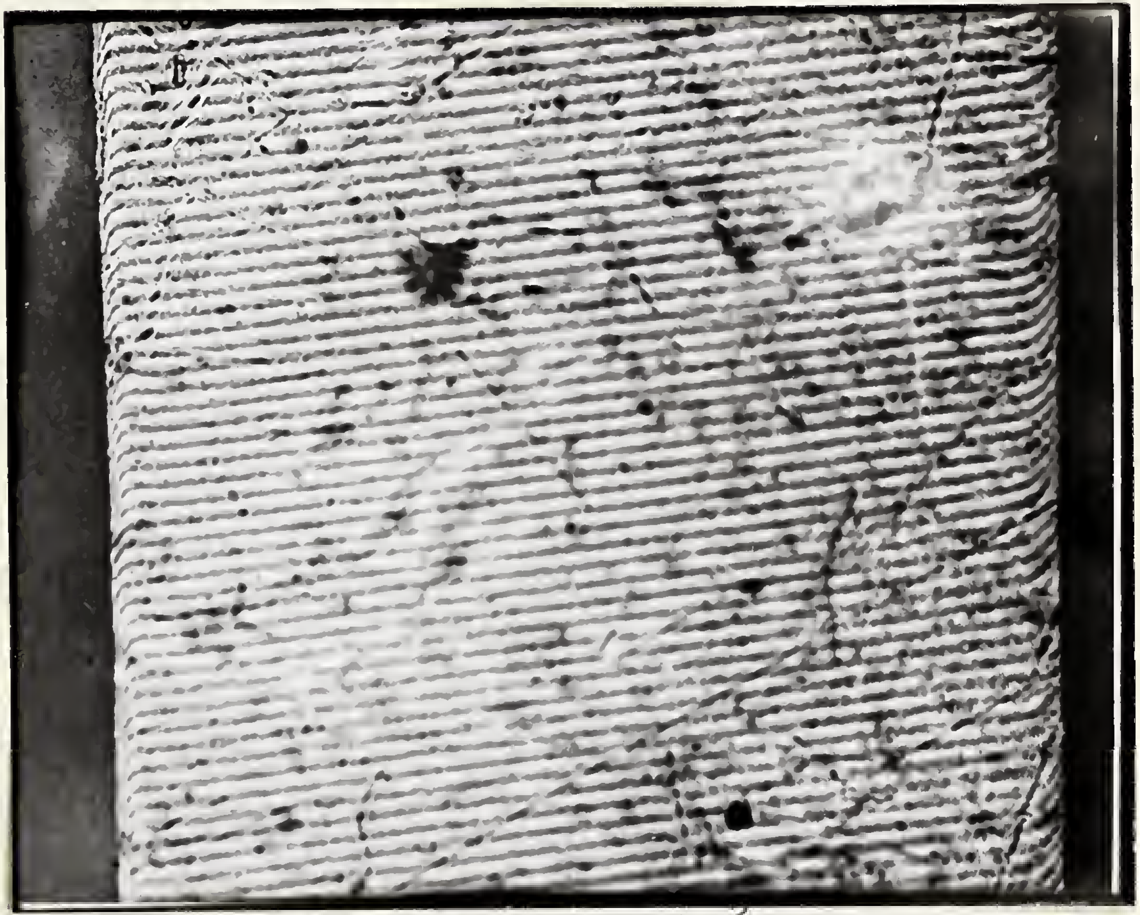
Electrodes less than 1.92 millimeters in thickness. Bath temperature 4°C.; solution temperature 7.5°C., 30 g/l.

Electrode thickness millimeters	Current density $\mu A/cm^2$	Anode shift λ_{Na_D}	Anode shift g/l
.25	1600	.28	2.72
	3200	.35	3.14
1.50	256	.32	.47
	768	.80	1.28
	1068	1.15	1.63
	1600	1.50	2.13
	2132	1.90	2.70

COMPARISON OF FRINGES AT DIFFERENT ELECTRODE THICKNESSES



CATHODE .25 mm. electrodes, 1600 μA/cm^2 7.5°C., 30 g/1 ANODE



2 mm. electrodes, 1600 μA/cm^2, 7.5°C., 30 g/1

these was extremely diffuse and could not be photographed properly. However, from the appearance of the fringe shifts, it is certain that the same gram/liter changes in concentration were observed. In the event that the pattern were a surface or convection effect, it would be the thinnest electrodes which would be expected to reveal a change, since here the proportion of surface is largest, and convection effects would be minimized. In the thick electrodes, the pattern undergoes a large change in clarity, but none in form.

The conclusion that the refractive index change is independant of the thickness of the electrodes is in agreement with Ibl[2].

While the values for lesser electrode thicknesses than 1.92 millimeters do not lie exactly on the line, they are as close to the best-fit line as are the data for the 1.92 millimeter electrodes. Larger experimental errors are inherent in the use of thinner electrodes, particularly the .25 millimeter ones, since a given fringe shift represents a concentration change larger by nearly a factor of 8 than the same fringe shift does when the 2-millimeter electrodes are used. Therefore, the expected experimental error is about a factor of 8

---

[2] N. Ibl and R. Müller, Z. Elektrochem., 59, 671-6 (1955)

larger. If any optical surface effect were present, it would be expected that the fringe shift would be relatively greater for the smaller electrodes where the surface/volume ratio is larger; this is not observed. The presence of convection would show a larger effect for thicker electrodes, in accordance with Ibl's equation given on page 5; again, this is not the case. It is therefore concluded that neigher convection nor optical surface effects play any large part in this work. For the balance of the investigation, 1.92 millimeter electrodes are used, since they provide the largest displacements in the interference fringes, yet give a clearly defined pattern.

The next study was that of the dependance of the measured fringe shift on the concentration of the solution. Solutions of concentrations 1, 10, 30 and 100 grams $CuSO_4$ per liter, and a saturated solution of $CuSO_4$ were studied. The data are shown in Table III. The marked difference between the anodic and cathodic fringe displacements in the 1 gram per liter solution is attributed to the effect of the concentration polarization itself; as the difference between the solution concentration in the diffusion layer and that in the bulk of the solution becomes large, a Nernst reverse potential is generated opposing further

change; and, of course, the decrease in concentration at the cathode cannot exceed the total concentration in the bulk of the solution; hence, at higher current densities, a large difference exists between the first wave at the anode and that at the cathode. (See figures VII and VIIA)

The cathodic diffusion layer can be clearly seen to be erratic, particularly at high current densities. Small changes in the tilt of the cell affect the cathode's apparent diffusion layer markedly, as, in accordance with Snell's law, the light is bent so that all of the fringes appear superimposed, giving an erratic result. For this reason few of the cathode results are treated in any detail; but it is nevertheless informative to note that no apparent "negative concentration" is attained. The concentration goes to zero and only zero at the bubble point. The results are shown in Figure VI for the anode, and the results for the cathode are in Figure VII.

It was considered desirable to determine the cathode values more precisely, so the 10, 30, and 100 gram/liter solution determinations were repeated, using an alternate technique. The figures shown in Table III arise from photographs taken with the microscope focused on the anode, and the tilt of the cell arranged so as to favorably display the diffusion layer about

TABLE III

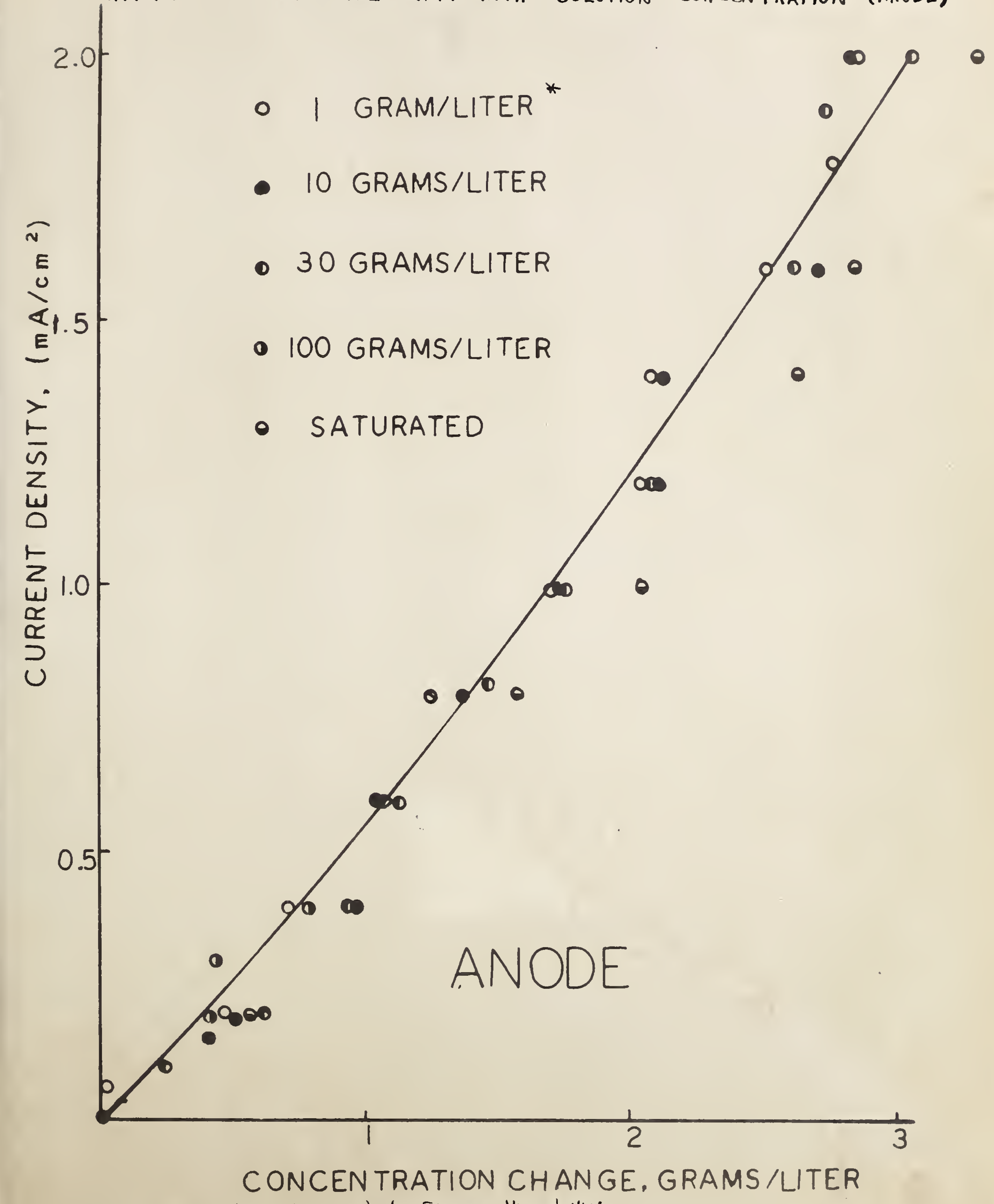
The variation of the first wave with concentration

Bath temperature, 4°C.; solution temperature 7.5°C.

Concentration grams/liter	Current density $\mu A/cm^2$	Anode shift g/l	Cathode shift g/l
1	0	0	0
	200	.45	.22
	400	.70	.56
	600	1.12	.93
	800	1.23	.93
	1000	1.68	.95
	1200	2.02	.985
	1400	2.04	1.01
	1600	2.58	1.01
	1800	2.72	.99
	2000	2.81	1.01
10	---	SEE TABLE I	---
30	0	0	0
	100	.13	.22
	200	.60	.73
	400	.96	.83
	600	1.07	.90
	820	1.43	1.25
	1000	1.73	1.10
	1200	2.02	1.57
	1600	2.46	2.82
	1800	2.68	1.89
	2000	3.03	2.34
	6000	5.10	?
	10000	7.28	?
100	0	0	0
	200	.39	.46
	300	.42	.57
	400	.77	.89
saturated	0	0	0
	200	.58	.54
	800	1.58	1.97
	1000	2.01	2.42
	1400	2.62	2.62
	1600	2.83	2.85
	2000	3.28	2.86

FIGURE VI

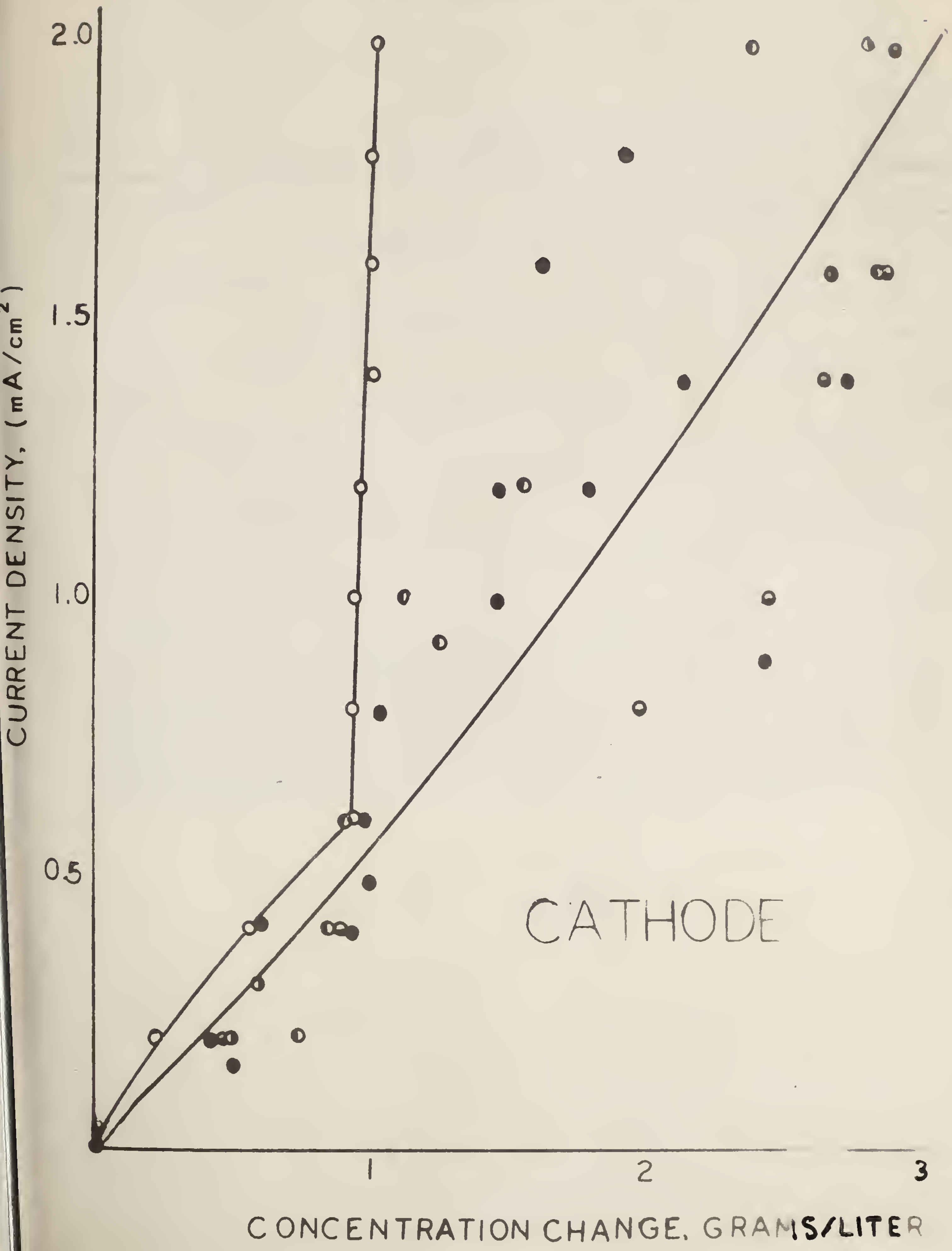
VARIATION OF FIRST WAVE SHIFT WITH SOLUTION CONCENTRATION (ANODE)



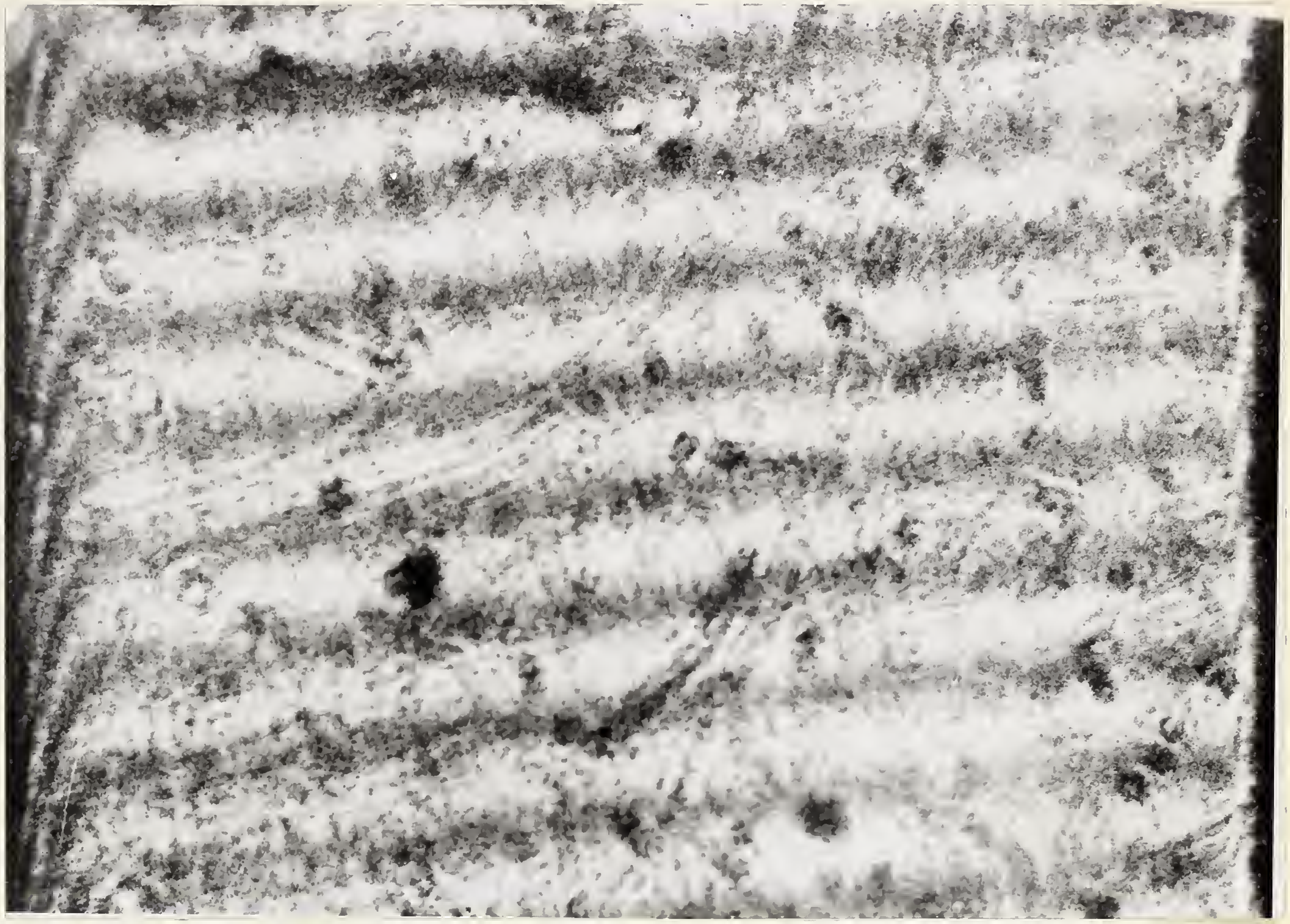
* These symbols also apply to Figures VII and VIIA

FIGURE VII

CONCENTRATION DEPENDANCE OF FIRST WAVE AT THE CATHODE
(FROM INTERFEROGRAM MEASUREMENTS)



INTERFEROGRAM SHOWING UNEQUAL FIRST WAVE SHIFTS AT ANODE AND CATHODE



ANODE 1 g/l, 1600 μA/cm^2, 7.5°C. CATHODE

the anode. To observe the cathode layer, a different focus is required--in fact, not all portions of this layer are clearly in focus at any one point. Therefore, measurements of the cathode layer were made visually with an eyepiece containing a reticule. This reticule was lined up with the general pattern of the fringe, then the focus changed to bring the cathode layer into focus, and the tilt of the cell adjusted to move the apparent diffusion layer further from the cathode; the furthest extent of the fringe was noted and the focus returned to the general pattern to ascertain that the reticule was still in alignment with the general pattern. This precedure gave results which are considered to be the best obtainable with a multiple-beam technique at the cathode. These results are shown in Table IV and Figure VIII.

Although there is a systematic trend in the points, producing larger fringe shifts with more concentrated solutions, one least-squares solution of all three runs is shown. The observed trend is in accordance with expectations, as the effect of the Nernst concentration potential becomes smaller with increasing concentration, and also because the diffusion constant decreases with increasing concentration, which would be expected to produce a larger concentration gradient in accordance with Fick's law of diffusion.

TABLE IV

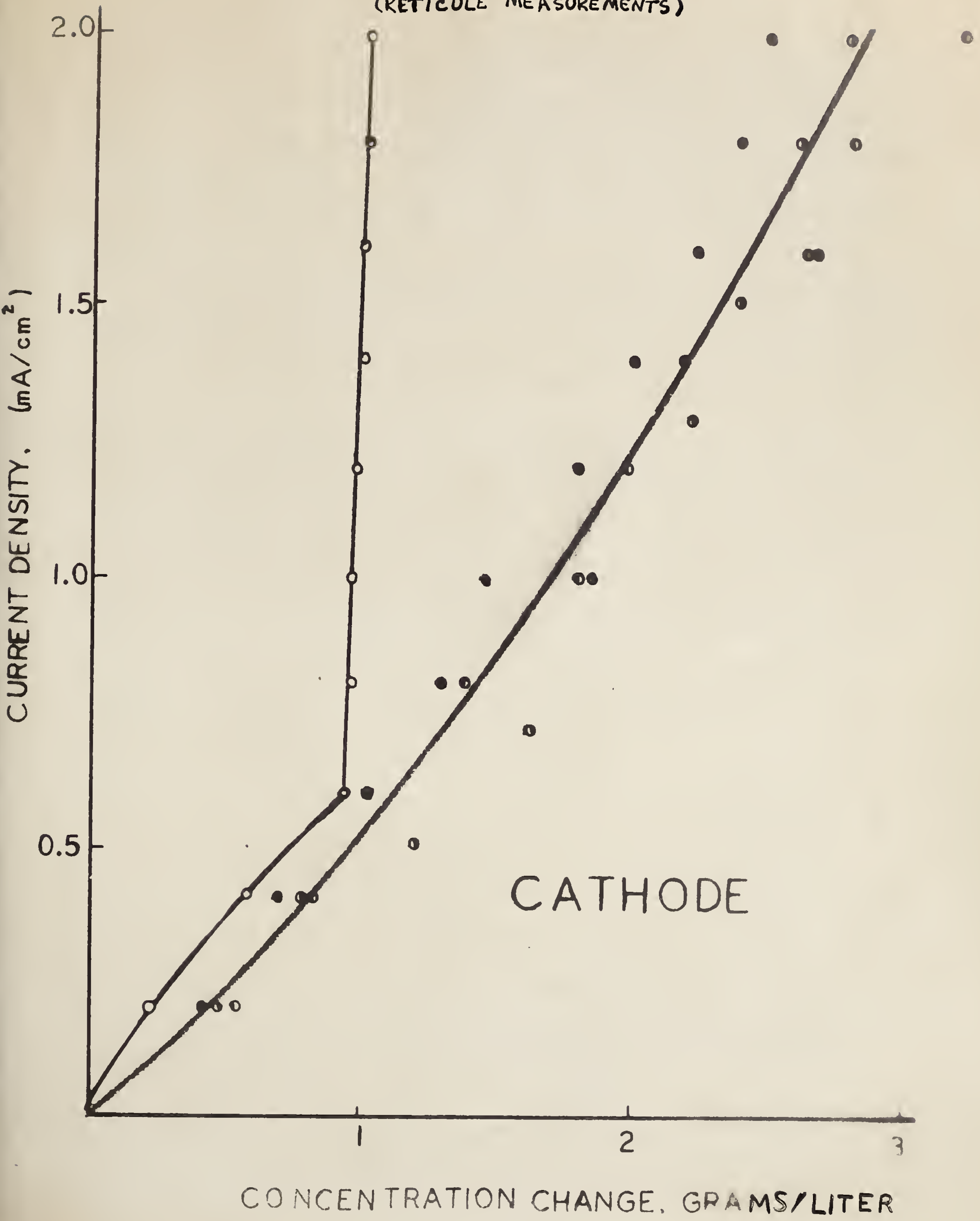
Reticule measurements of the first wave at the cathode

Bath temperature, 4°C.; solution temperature 7.5 degrees C.

Concentration grams/liter	Current density $\mu A/cm^2$	Cathode shift grams/liter
10	0	0
	200	.40
	400	.68
	600	1.00
	800	1.26
	1000	1.41
	1200	1.78
	1400	1.98
	1600	2.20
	1800	2.36
	2000	2.46
30	0	0
	200	.50
	400	.80
	800	1.36
	1000	1.76
	1200	1.95
	1400	2.16
	1600	2.60
	1800	2.80
	2000	3.20
100	0	0
	200	.45
	400	.76
	500	1.20
	700	1.60
	1000	1.82
	1300	2.20
	1500	2.35
	1800	2.60
	2000	2.80

FIGURE VII~~I~~

CONCENTRATION DEPENDANCE OF FIRST WAVE AT THE CATHODE
(RETICULE MEASUREMENTS)



The effect of the reflectivity of the flats was studied, using flats of 40%, 50%, and 90% reflectivity. The 40% reflectivity gave poorly defined fringes, so that only three of the points were measurable, but the other two pairs of flats gave fine fringes, although quite different from one another in character. The data obtained is shown in Table IV, and a graph of the results is given in Figure VIII.

The least-squares solution of the points, assuming an exponential curve, is

$$C = 1050\ G^{1.41} \qquad (3,4)$$

The manner in which the data scatter is quite random, so it is concluded that the results are not affected by a change in the reflectivity of the flats.

At this point it should be pointed out that the appearance of the photographs does depend on the reflectivity of the flats. Should it become necessary to obtain good interferograms of the pattern about the cathode, 40% or 50% reflecting flats would be desirable. In this work, however, the majority of the runs were performed using the 90% reflecting flats, as the dark line between the two light ones made an ideal spot at which to make measurements. But since the light is reflected between the two flats an average of more times, the effective number of interferring beams is increased; any tilt of the cell increasing the

extent of refraction toward the less-dense solution at the cathode makes the pattern at the cathode virtually unmeasurable. The patterns about the two electrodes are basically similar, and for the purpose of this work, visual measurement with the reticule of the cathode seemed adequate. The anode has been the subject of concentration since it is inherently easier to measure with a multiple beam apparatus.

The optical arrangement may be varied by using the reflection rather than the transmission method. For the reflection method, the position usually occupied by the 45° mirror is occupied by a half-silvered mirror, also placed at a 45° angle, although at right angles to the usual position of the normal mirror (FigureIIB). The cell is now placed below the mirror as shown in chapter 2.[3]

A run was performed in this manner using 1.92 millimeter electrodes, one 90% reflecting flat on the bottom, below the solution, and one 50% reflecting flat above the solution. Both the temperatures of the bath and the solution were 28°C. The results are given in Table V.

The least squares exponential equation for these data is essentially the same as for the reflectivity-dependance runs; the points lie among those of the previous results. Although these points were obtained at 28° C. and the

---

[3] See page 12

TABLE IV

The variation of the first wave with the optical reflectivity of the flats. Bath and solution temperature, 30°C., 30 grams $CuSO_4$ per liter

Reflectivity %	Current density $\mu A/cm^2$	Anode shift λ_{Na_D}	Anode shift g/l	Cathode shift λ_{Na_D}	Cathode shift g/l
40	0	0	0	0	0
	200	.45***	.51***	.45 ***	.51***
	400	.68***	.73***	.56 ***	.63***
	600	.97***	1.09***	.74***	.83***
	1000	.90	1.01	.99***	1.11***
	1400	1.18	1.32	1.21***	1.38***
50	0	0	0	0	0
	200	.28	.33	.28	.33
	400	.12* .44***	.13* .49***	.97	1.09
	600	.60	.67	1.20	1.34
	800	.78	.88	1.55	1.75
	1200	.97	1.09	2.06	2.32
	1600**	1.00	1.12	1.80	2.02
	1800	1.30	1.46	1.32***	1.48***
	2000	1.50	1.68	3.00	3.36
90	0	0	0	0	0
	200	.35	.39	.35	.39
	400	.43	.48	.60***	.72***
	600	.54	.61	.70***	.83***
	800	.60	.72	.88***	.98***
	1000	.86	.96	.94***	1.05***
	1200	1.06	1.19	1.08***	1.21***
	1600	1.27	1.42	1.39***	1.55***
	1800	1.32	1.48	1.51***	1.69***
	2000	1.40	1.57	1.90***	2.70***

* data omitted from calculations because of its large deviation from other results. No explanation is obvious.

** A poor photograph. Camera or cell moved.

*** Graticule visual measurement. No photograph taken.

reflectivity points were obtained at 30°, the 2° temperature difference is apparently not sufficient to be discernable here.

These results are also shown in Figure VIII.

TABLE VI

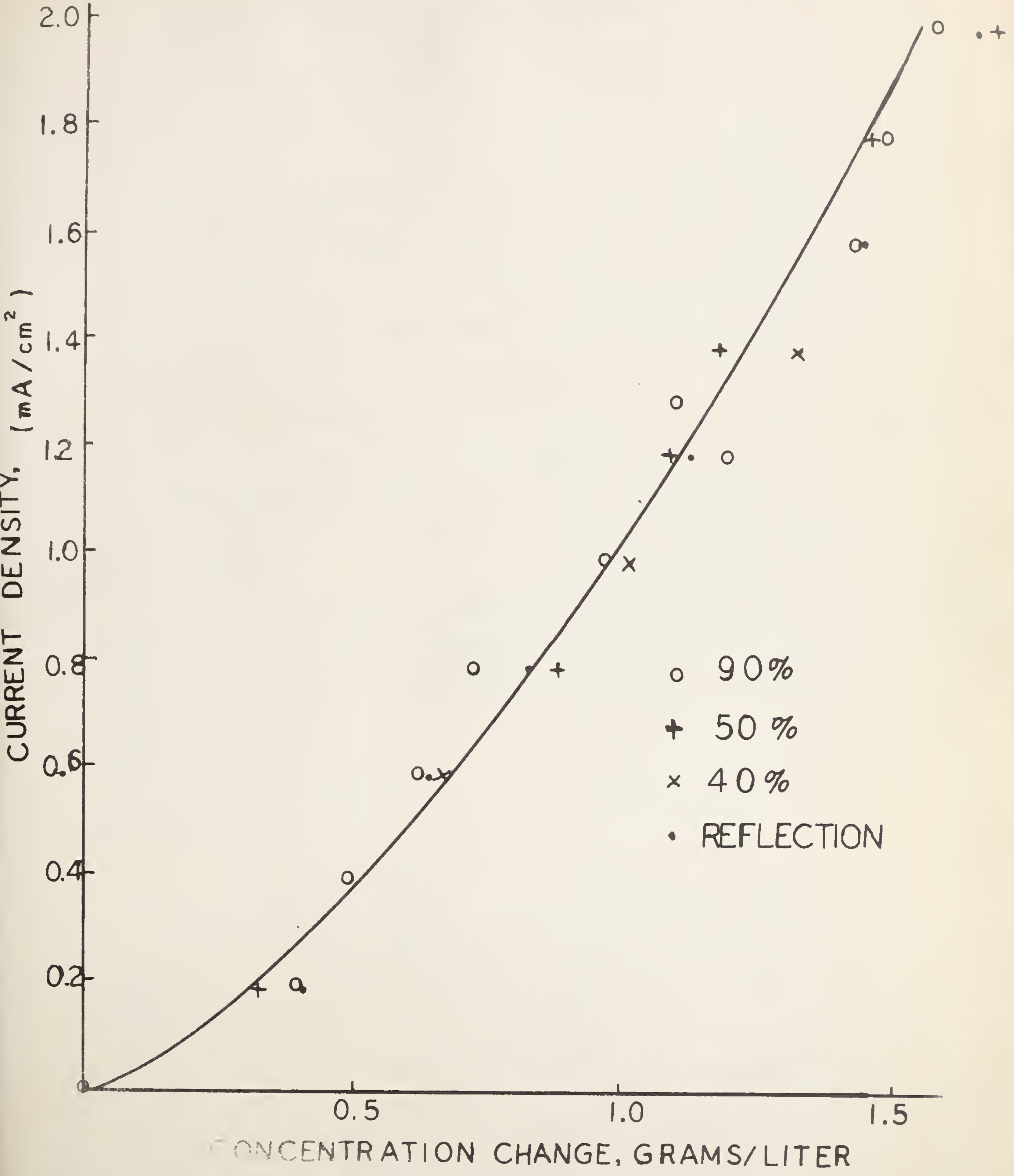
REFLECTION TECHNIQUE

Current density μA/cm^2	Anode shift λ_{Na_D}	Anode shift g/l	Cathode shift λ_{Na_D}	Cathode shift g/l
0	0	0	0	0
200	.28	.31	.33	.37
400	.41	.46	.41	.46
600	.58	.65	.64	.71
800	.74	.83	.97	1.09
1000	.86	.96	(.46*)	
1200	1.00	1.12		
1600	1.28	1.44		
2000	1.48	1.65		

* this and higher-current-density photographs are so badly focused at the cathode that the measurement is meaningless.

DEPENDANCE OF FIRSTWAVE ON REFLECTIVITY OF THE OPTICAL FLATS

FIGURE VIII



PART III. Temperature dependance of the first wave.

In this section of the investigation, a series of runs were performed on a 10 gram per liter solution, using 1.92 millimeter electrodes, the transmission method, and controlling the temperature at several different temperatures. Since the bath temperatures and the true temperature of the solution proved unequal in some cases, the temperature in such cases will be given with the true temperature first, followed by the bath temperature in parentheses, when this differs from the true temperature.

The data obtained at 7.5° (4) and 30° have already been presented. The additional data obtained are shown in Table VI. Some photographs of the 7.5° (4°) interference pattern follow Table VI.

Some of the results obtained for the anode are shown in Figure IX. The least squares solutions of the points at 7.5° (4°) and 30° have already been given. At 15°, the solution is

$$C = 1040\ G^{.98} \qquad (3,5)$$

and at 42° (45°)

$$C = 1670\ G^{1.10} \qquad (3,6)$$

Figure X shows a graph of fringe shift against temperature at constant current density for several current densities.

TABLE VII

The temperature dependance of the first wave in a 10 grams per liter solution of $CuSO_4$

Current density $\mu A/cm^2$	Temperature °C	Anode shift λ_{Na_D}	Cathode shift λ_{Na_D}
0	6 (1)	0	0
100		.12	0
200		.56	.23
400		.90	.60
600		.98	.70
800		1.24	1.41
1000		1.68	1.34
1200		1.80	2.25
1400		2.20	?
1600		2.85	?
0	8.3 (9)	0	0
40		0	0
500		.40	.45
1000		1.20	1.20
0	13.5	0	0
100		.27	.27
200		.34	.45
400		.54	.81
600		.70	.99
800		.80	1.47
0	19.8	0	0
450		.53	.66
0	25.5	0	0
100		0	0
200		.05	.05
300		.50	.66
0	15	0	0
100		.067	.27
200		.27	.50
400		.41	.82
600		.54	1.03
800		.73	1.46
1000		.97	1.66
1200		1.00	1.50
1400		1.25	1.50

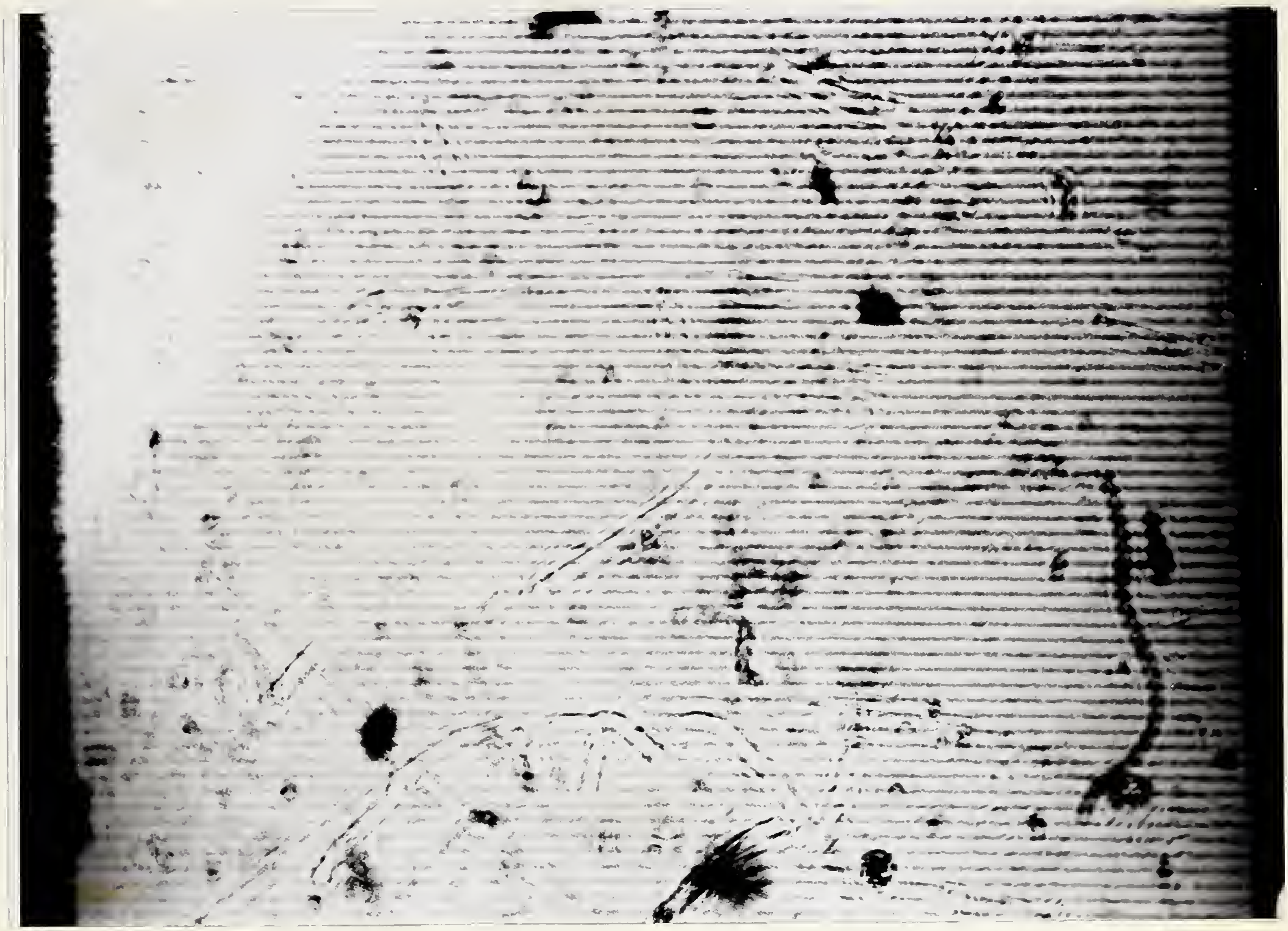
TABLE VII, cont.

1600	15	1.45	1.75
2000		1.75	2.50
0	35	0	0
200		.28	.28
250		.43	.56
800		1.02	1.02
1000		1.20	1.54
0	39 (40)	0	0
150		0	.22
250		0	.35
400		.57	.82
1000		.68	.85
2000		1.15	1.54
0	42 (45)	0	0
200		0	.23
400		.26	.26
600		.40	.32
800		.62	.41
1200		.80	.72
1500		.93	1.23
2000		.97	1.40
0	46 (50)	0	0
200		.04	0
1400		.81	1.43
2000		.84	1.69
0	50 (55)	0	0
400		0	.14

(this run could not be finished as the plasticene had become too soft to support the cell and the fringes would no longer remain in focus.)

A SERIES OF INTEROGRAMS SHOWING THE EFFECT OF INCREASING CURRENT DENSITY

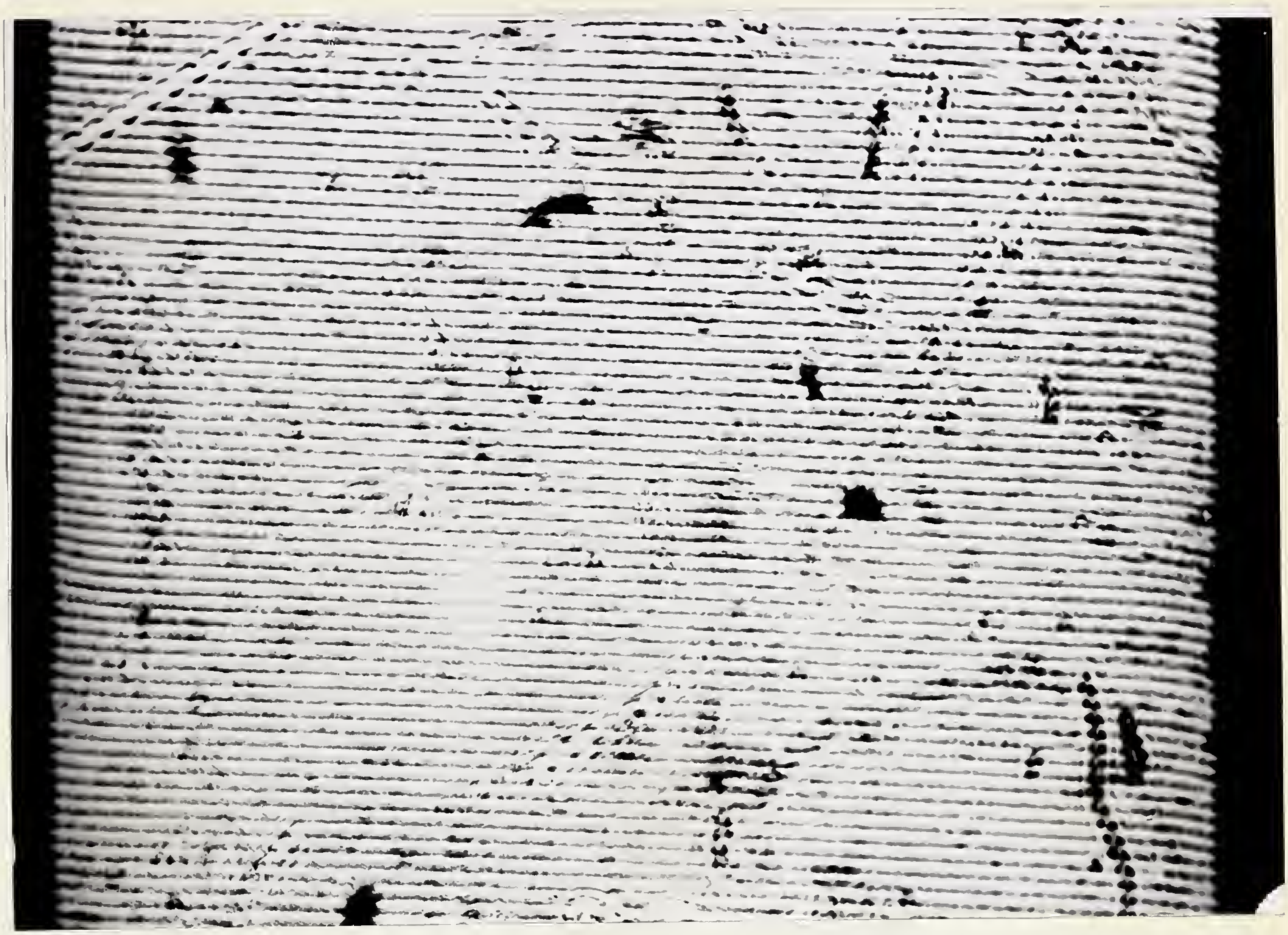
INTERFEROGRAM #1



10 g/1 $CuSO_4$, no current, 7.5° (4°) C.

A SERIES OF INTERFEROGRAMS SHOWING THE EFFECT OF INCREASING CURRENT DENSITY

INTERFEROGRAM #2



10 g/l $CuSO_4$, 200 µA/cm^2, 7.5° (4°) C.

CATHODE

ANODE

A SERIES OF INTERFEROGRAMS SHOWING THE EFFECT OF INCREASING CURRENT DENSITY

INTERFEROGRAM #3

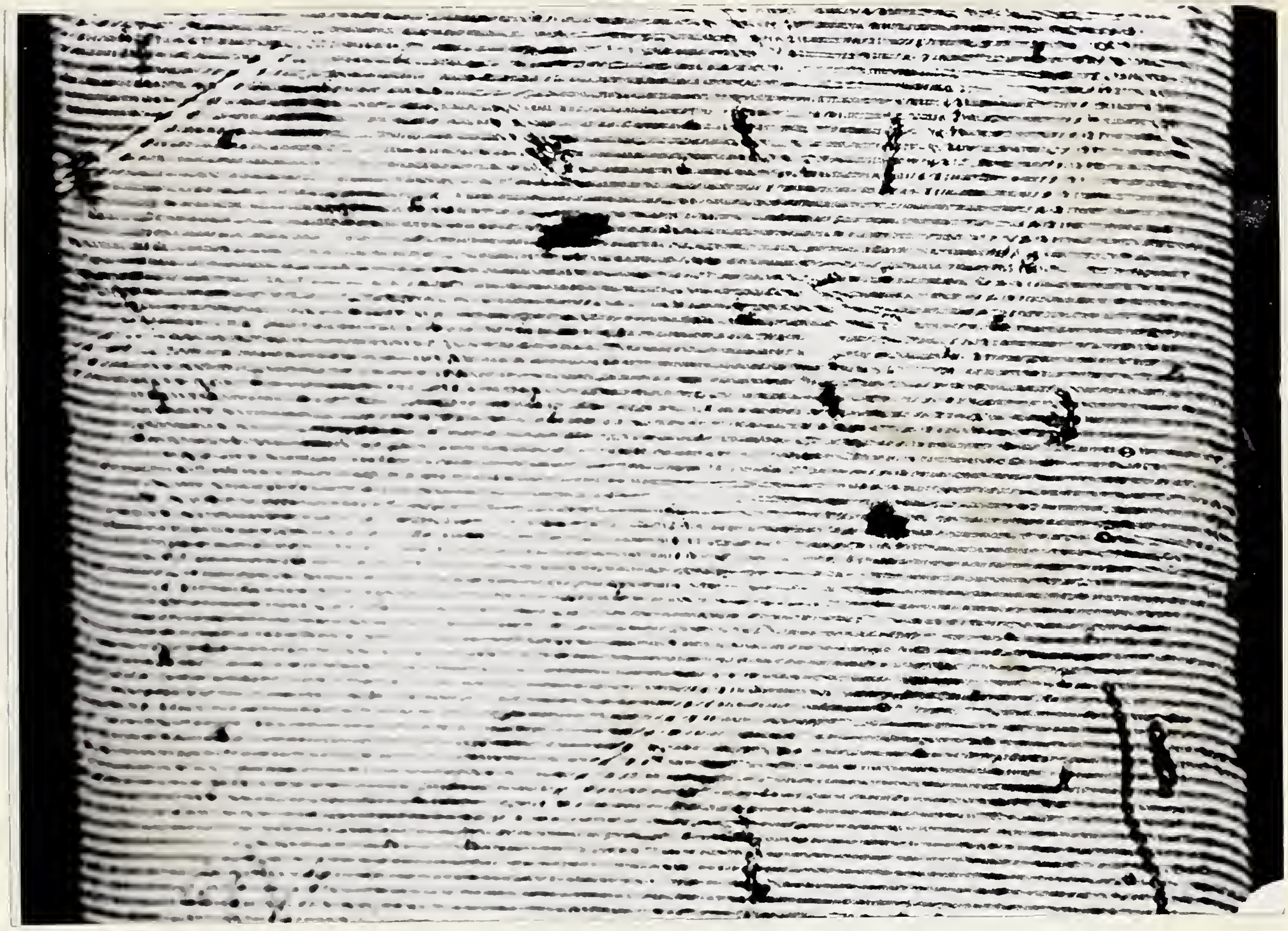
10 g/l $CuSO_4$, 400 μA/cm^2, 7.5° (4°) C.

CATHODE

ANODE

A SERIES OF INTERFEROGRAMS SHOWING THE EFFECT OF INCREASING CURRENT DENSITY

INTERFEROGRAM #4



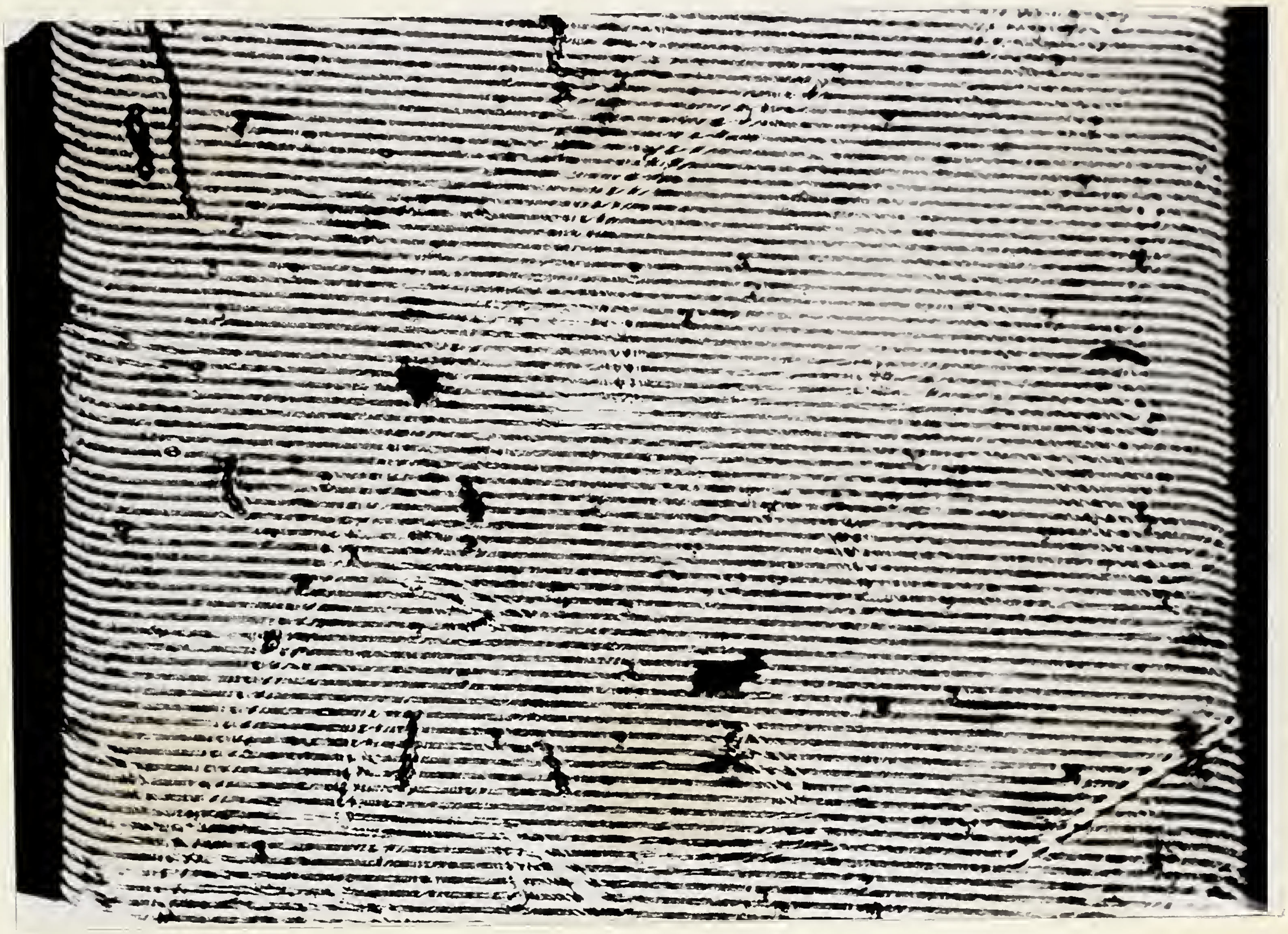
10 g/l $CuSO_4$, 600 μA/cm^2, 7.5°(4°) C.

ANODE

CATHODE

A SERIES OF INTERFEROGRAMS SHOWING THE
EFFECT OF INCREASING CURRENT DENSITY

INTERFEROGRAM #5



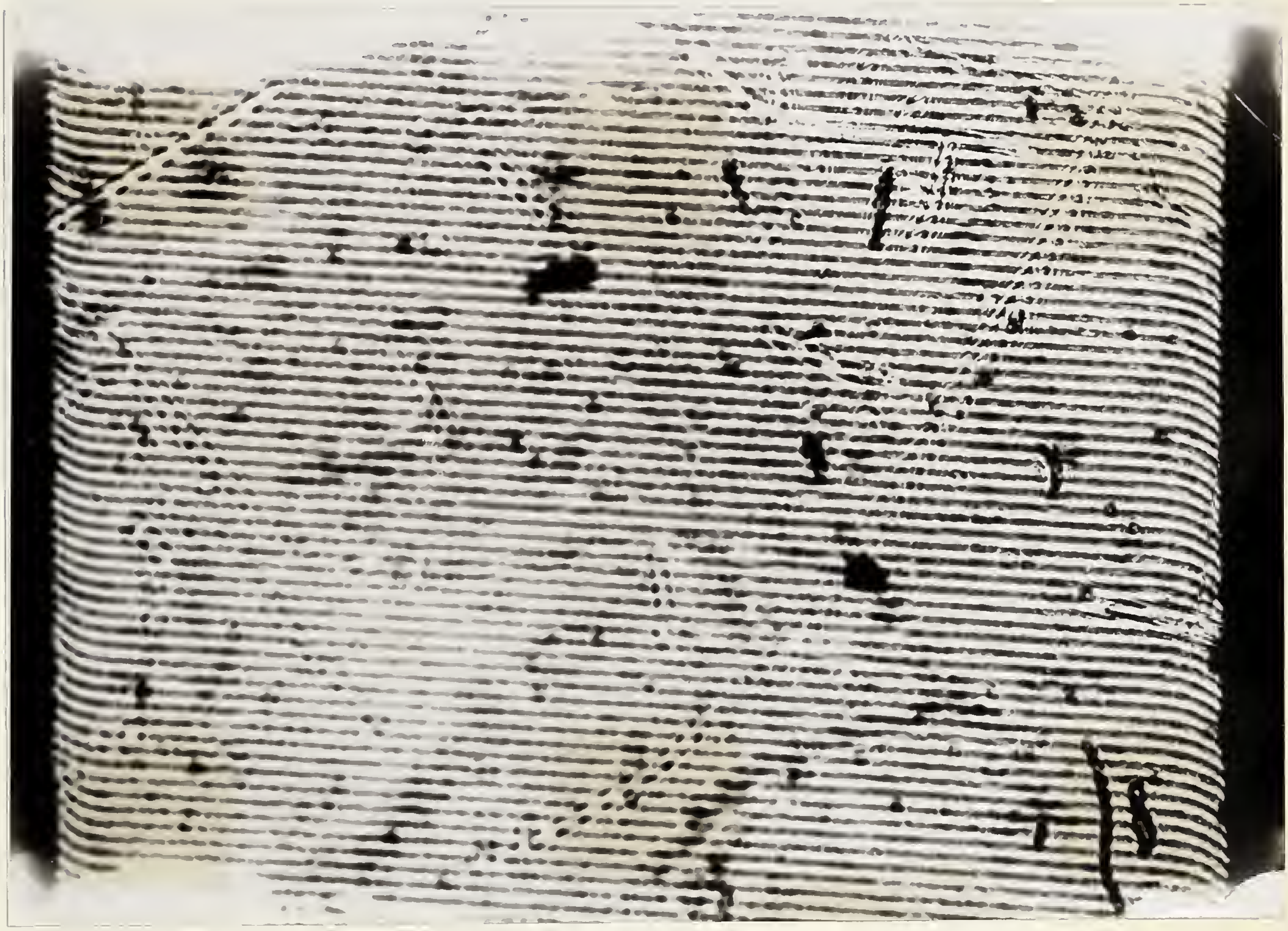
10 g/1 $CuSO_4$, 800 µA/cm^2, 7.5°(4°) C.

CATHODE

ANODE

A SERIES OF INTERFEROGRAMS SHOWING THE EFFECT OF INCREASING CURRENT DENSITY

INTERFEROGRAM # 6



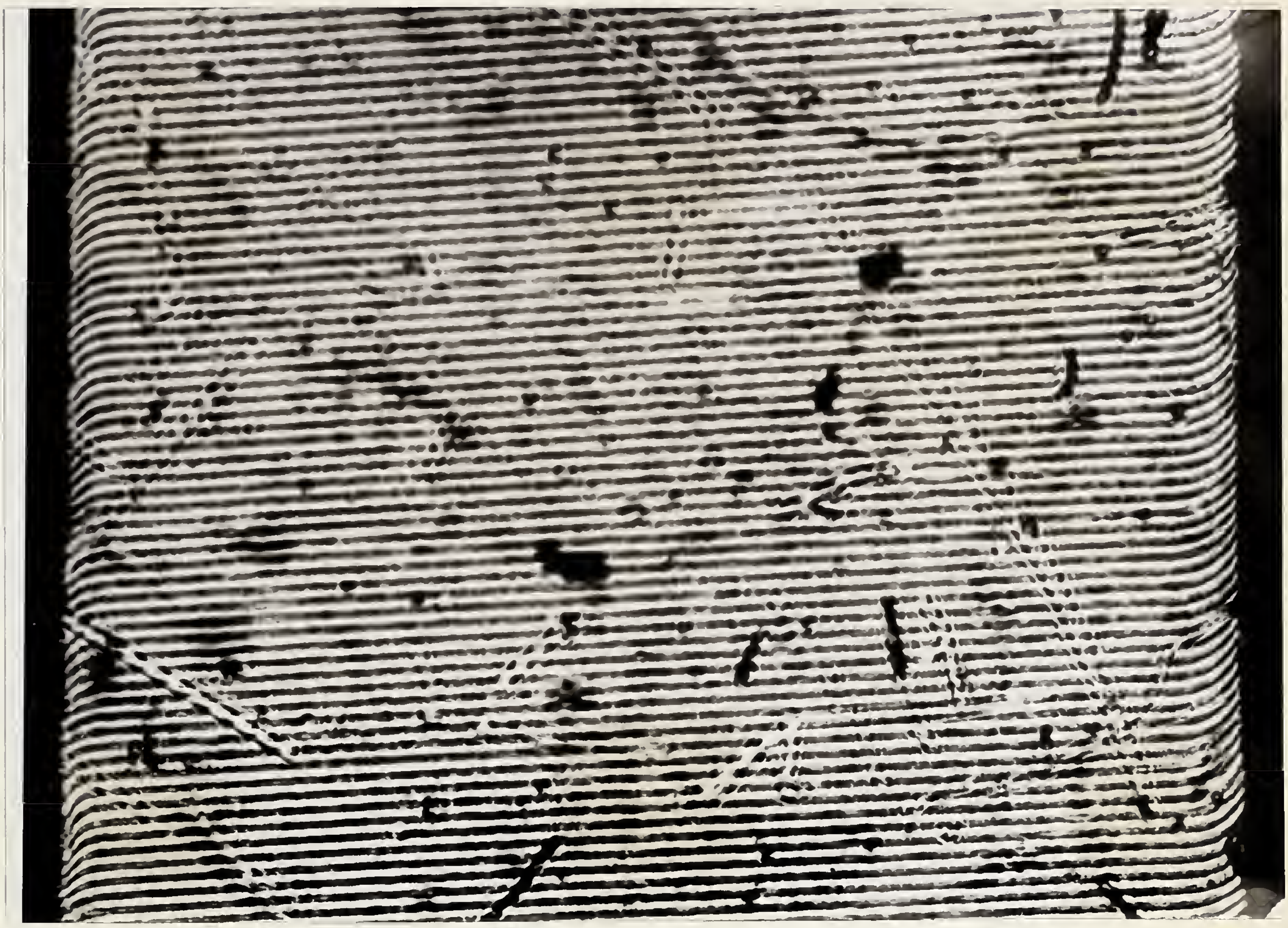
10 g/l $CuSO_4$, 1000 µA/cm^2, 7.5°(4°) C.

CATHODE

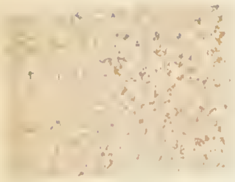
ANODE

A SERIES OF INTERFEROGRAMS SHOWING
THE EFFECT OF INCREASING CURRENT DENSITY

INTERFEROGRAM #7



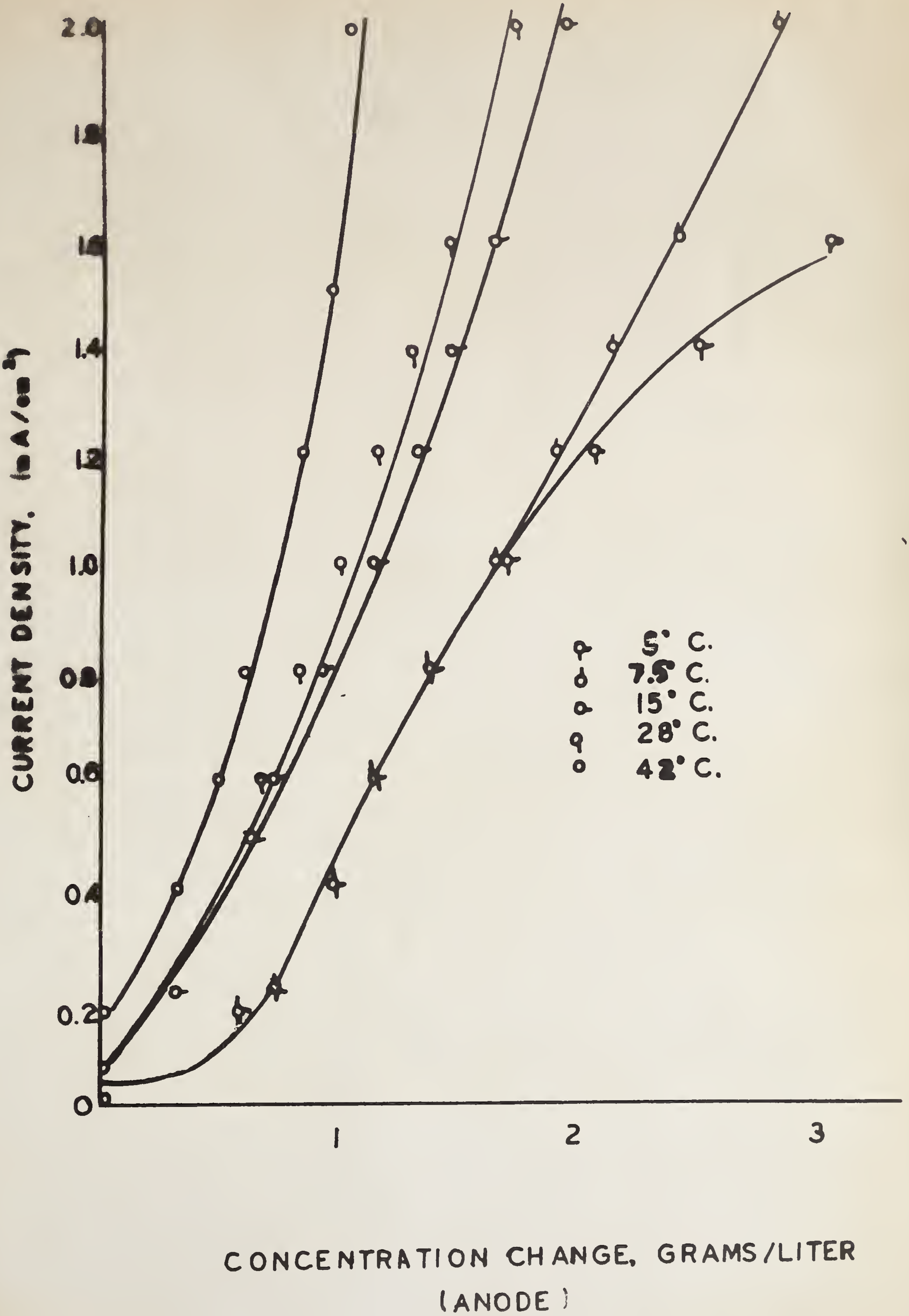
CATHODE 10 g/1 $CuSO_4$, 1400 μA/cm^2, 7.5°(4°)C. ANODE



[illegible]

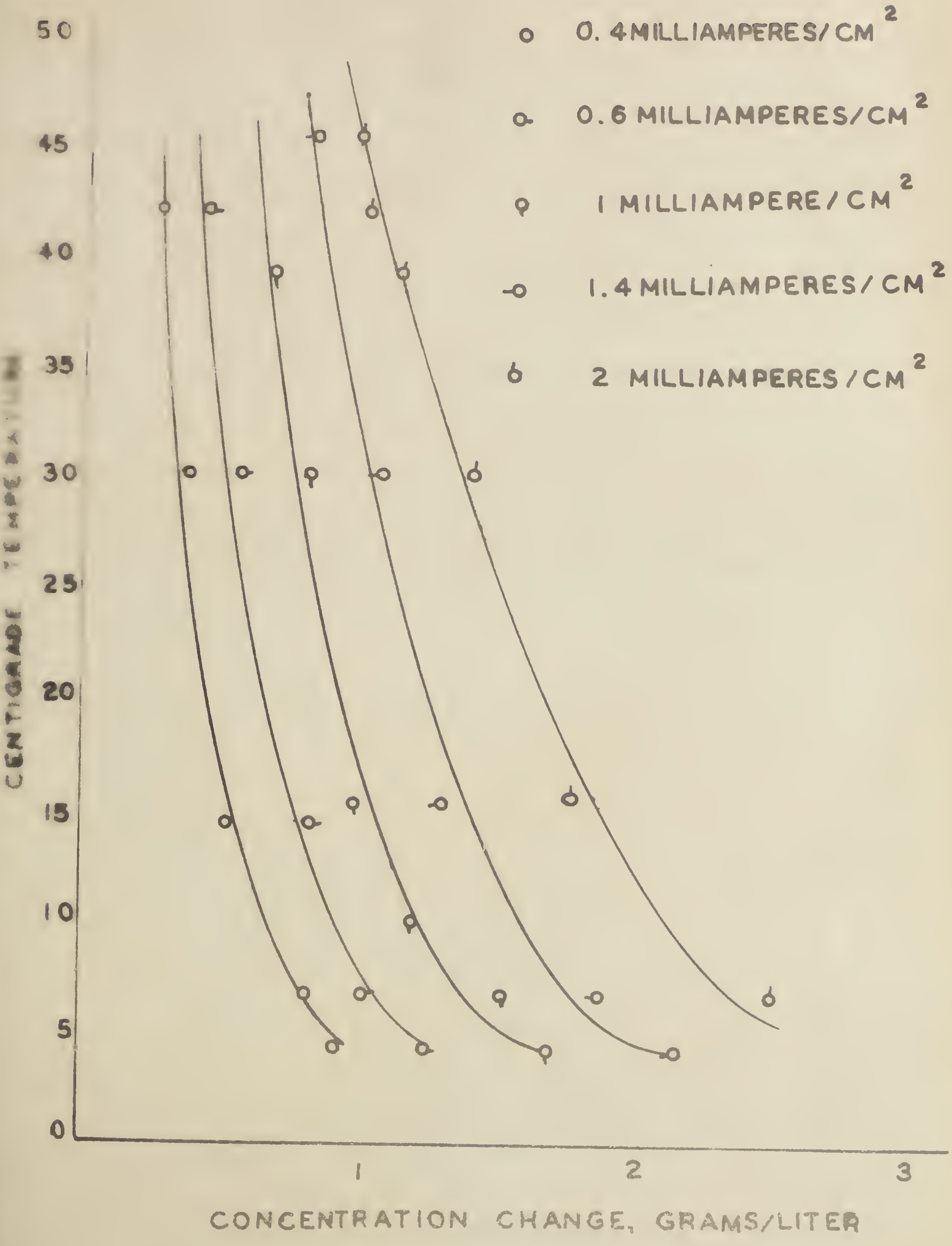
THE EFFECT OF TEMPERATURE ON CONCENTRATION CHANGE WITH CURRENT DENSITY

FIGURE IX



THE EFFECT OF TEMPERATURE ON CONCENTRATION CHANGE AT CONSTANT CURRENT DENSITY

FIGURE X



It is observed that a certain current density is attained before any concentration polarization is observed. This threshold current density increases with temperature, in the manner shown in Figure XI. The photographs on page 66 are interferograms taken as closely as possible to the threshold current density at 6° (1°) and 42° (45°).

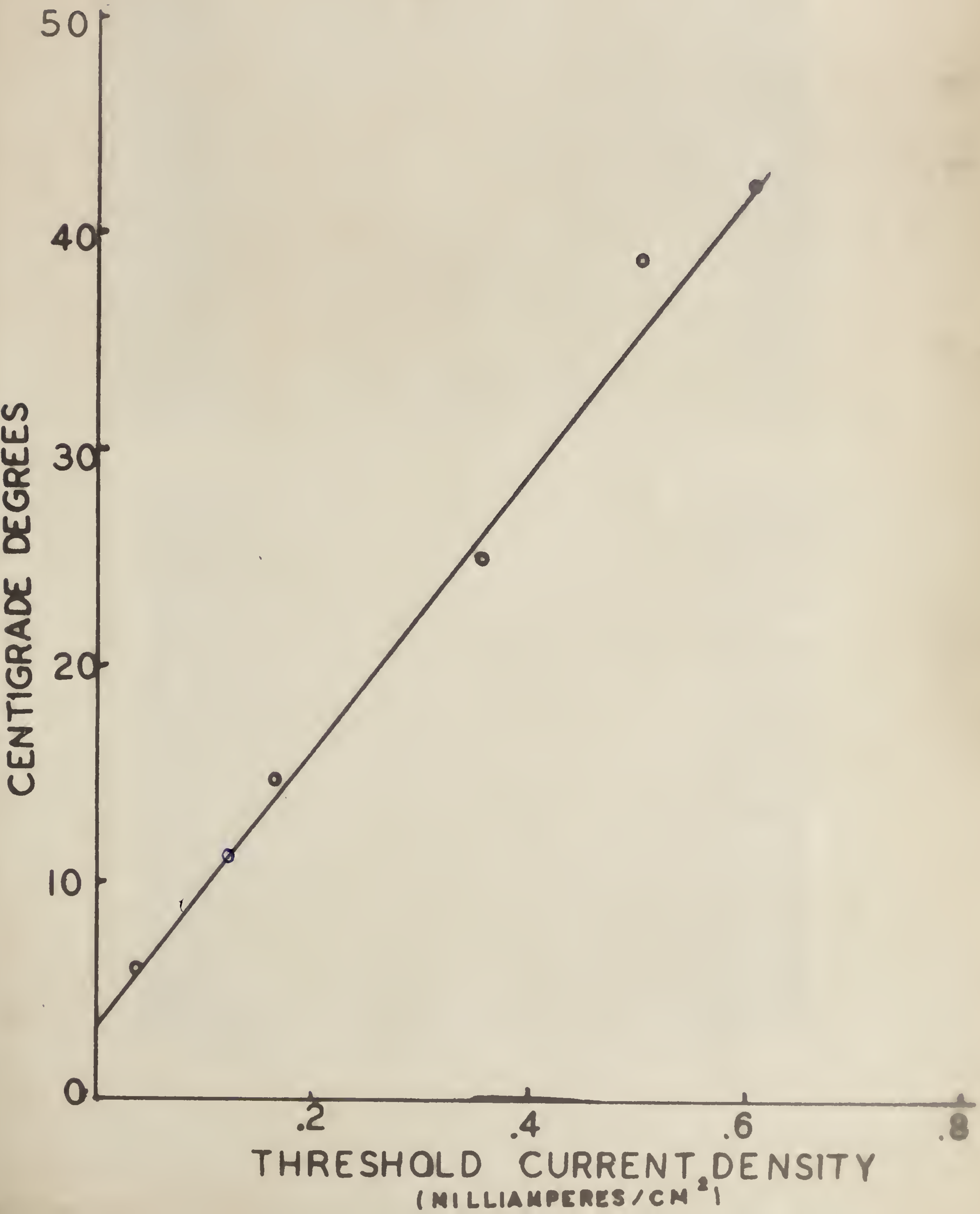
This threshold current density probably represents the amount of current which can be carried by the water; the work of Schuldiner and Hoare[4] indicates that it may be possible for this amount of current to be carried by the diffusion of protons through the metal of the electrode. The relationship is probably an exponential one in that case, although it appears as a straight line from the data obtained.

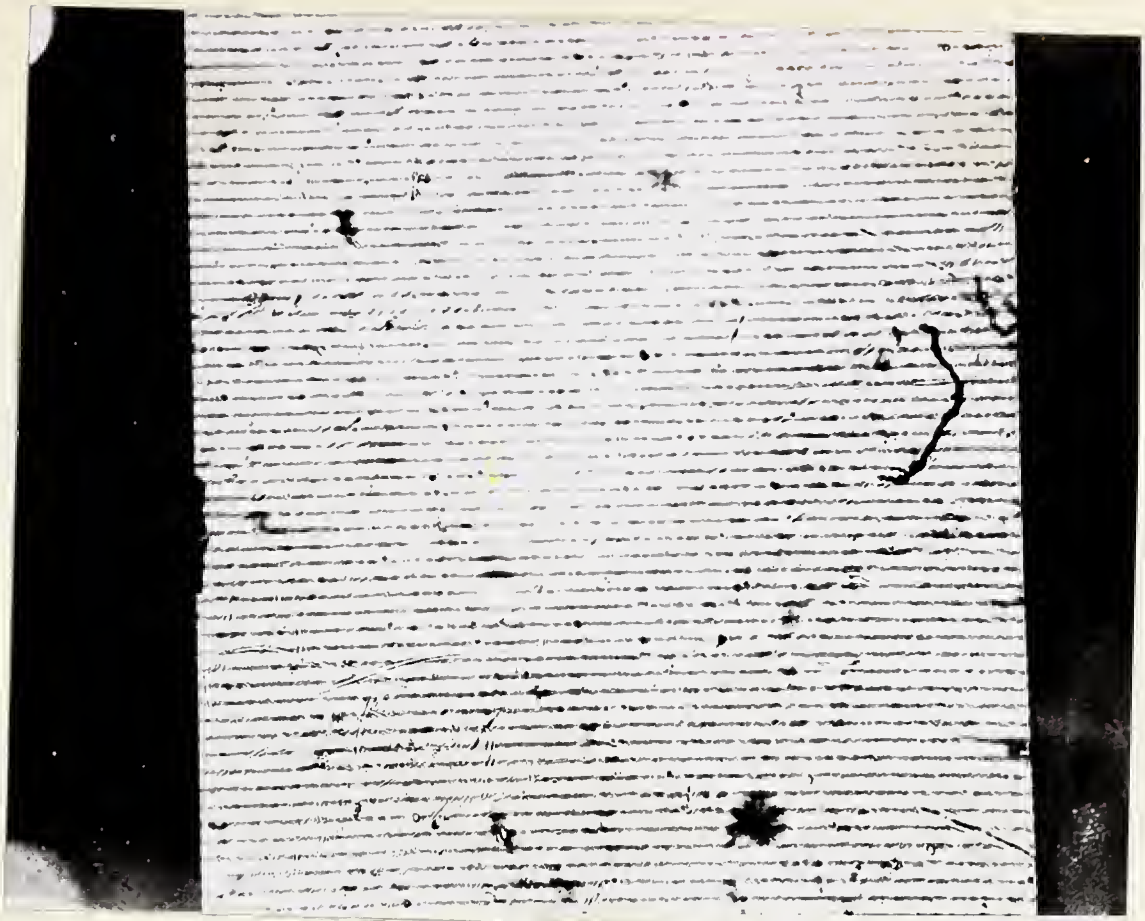
---

[4] Sigmund Schuldiner and James P. Hoare, Can. J. Chem., 37, 228 (1959)

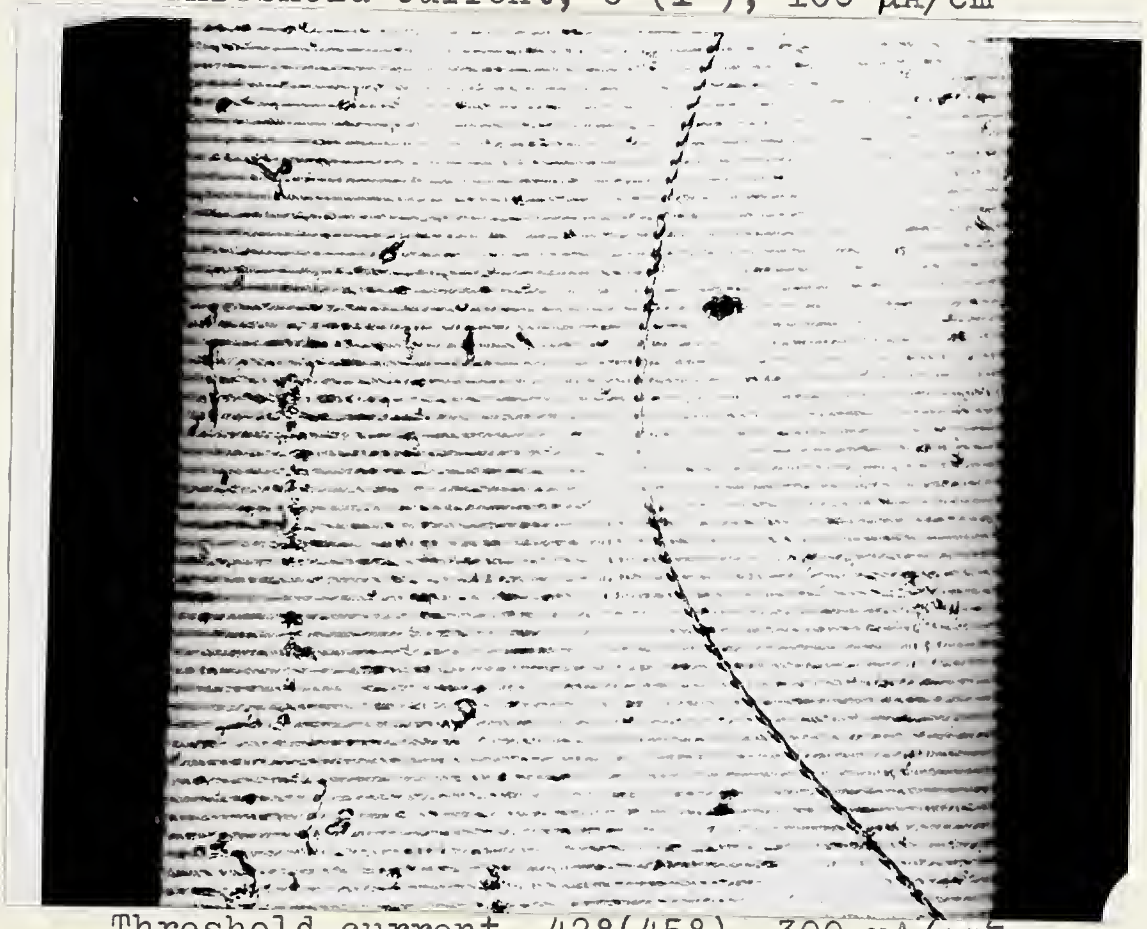
FIGURE XI

THE EFFECT OF TEMPERATURE ON THE CURRENT DENSITY AT WHICH THE ONSET OF CONCENTRATION POLARIZATION OCCURS





Threshold current, 6°(1°), 100 $\mu A/cm^2$



Threshold current, 42°(45°), 300 $\mu A/cm^2$

Part IV. The effect of electrode separation

This study was made with a solution containing 30 grams $CuSO_4$ per liter of solution, at a temperature of 8°(6°) C., using 1.92 millimeter electrodes and the transmission method. In these runs, the Lucite spacers between the electrodes were removed, and the electrodes adjusted to a desired spacing without their assistance. This meant that the electrodes had to be adjusted parallel without the help of the spacers. This was accomplished by pulling and twisting on the external electrical connections. The photographs showed that the electrodes were parallel within a degree or two. The actual current densities given are all somewhat smaller than they should be, since no correction was made for the now-exposed wedge in the electrodes.

Since the portion of the electrode having the wedge is obscured from the microscope by the Teflon rings, it could not be determined whether current was passing in the wedge region, or to what extent, by the fringe shift. After the run was completed, a deposit was found on this portion of the cathode for the first time.

Careful readings of voltage were taken, and care was taken to insure that there should be no bubbles present. The results are given in Table VIII and Figure XII.

The runs were performed by taking the photographs in

TABLE VIII

The dependance of first wave shift on electrode separation at 8°(6°) C.

Electrode separation millimeters	Current density mA/cm^2	Anode shift λ_{Na_D}	Anode shift g/l	Voltage volts
.11	0	0	0	0
	0.4	0.50	0.56	.04965
	0.8	0.65	0.73	.10364
	1.2	0.73	0.82	.12503
	1.6	1.23	1.38	.13234
	2.0	1.37	1.54	.14229
.30	0			0
	0.4			.07540
	0.8			.11643
	1.2			.13501
	1.6			.15337
	2.0			.17221
.40	0			0
	0.4			.07897
	0.8			.11926
	1.2			.13964
	1.6			.15952
	2.0			.17915
.54	0			0
	0.4			.08240
	0.8			.11832
	1.2			.13535
	1.6			.15955
	2.0			.17932
.65	0			0
	0.4			.07925
	0.8			.11884
	1.2			.13340
	1.6			.16036
	2.0			.17883

TABLE VIII, cont.

.70	0			0
	0.4			.08727
	0.8			.13517
	1.2			.15956
	1.6			.18184
	2.0			.19073
.75	0	0	0	0
	0.4	0.63	0.71	.08728
	0.8	0.78	0.87	.13580
	1.2	1.20	1.37	.16075
	1.6	1.62	1.81	.18196
	2.0	1.82	2.04	.19815
.90	0			0
	0.4			.09045
	0.8			.13249
	1.2			.15798
	1.6			.18222
	2.0			.19966
1.8	0	0	0	0
	0.4	0.73	0.81	.10339
	0.8	1.23	1.38	.13461
	1.2	1.43	1.60	.15936
	1.6	1.87	2.09	.17955
	2.0	2.00	2.24	.19930
3.0	0	0	0	0
	0.4	0.87	0.98	.16228
	0.8	1.17	1.31	.17880
	1.2	1.77	1.98	.19210
	1.6	2.34	2.26	.19509
	2.0	2.43	2.72	.22293

order of increasing current density as usual; after all photographs had been taken, the current density was again decreased through the points passed, and duplicate voltage readings taken; then the current was again increased, and voltages recorded a third time. The values given in Table VII are the averages of the three readings. Variations were of the order of .001 volts, and attributable to failure to adjust the current density to exactly the same value each time, a limitation of the micro-ammeter. Following these readings, the voltage was raised to a value just below the bubble point to ascertain whether the concommitant higher currant density would produce a second wave. In the case of all electrode separations of .65 millimeter and less, no second wave was formed. In the case of .75 and all higher electrode separations, the second wave did form. The .70 millimeter separation is uncertain. The second wave appeared to form over a part of the surface of the electrode in that case.

There are several interesting features concerning these runs as compared to the previous ones; at the small electrode separations, the first wave is smaller in both magnitude and in width (that is, it does not extend as far into the solution) although the gradient remains the same; for the .11, .30, and .40 millimeter electrode separations, the usual pattern coalesced into an S-curve and the measurements, rather than being made separately at each electrode, had to

be made on the fringe as a whole, then divided by two, introducing the assumption that both electrode waves were equal, which undoubtedly is not strictly true.

As the electrodes are moved closer to one another, the length of the conductance path in the solution decreasing, it would be expected that the resistance of the solution should also decrease, and that consequently less voltage should be required to produce the same current density. While this is true in a comparison of the 3.0 millimeter set of values to the other values, it does not seem to be true at smaller electrode separations. It would therefore appear that the conductivity does not remain constant (mhos/mm) but decreases with distance.

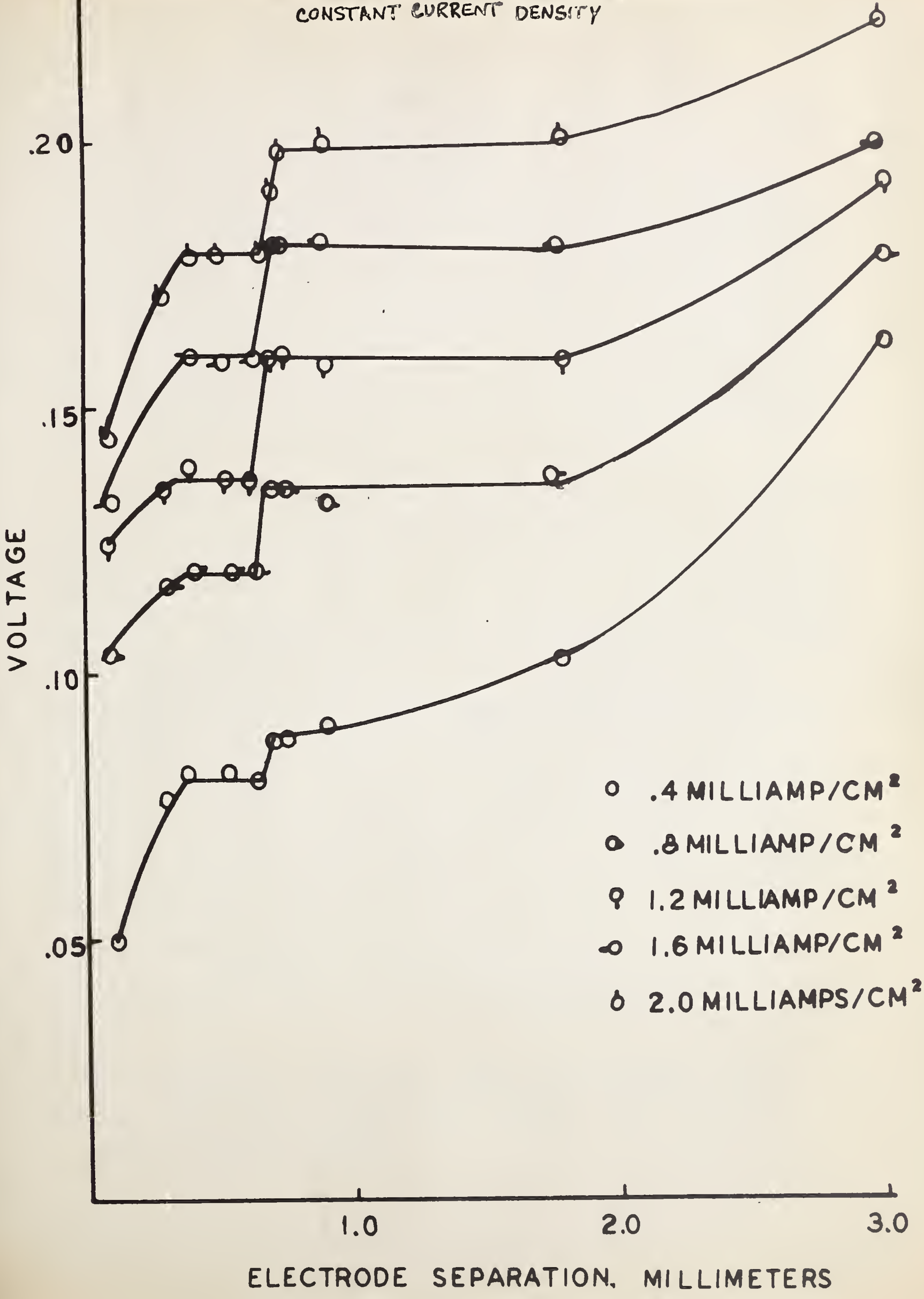
There is a distinct although small decrease in voltage required to produce a given current density exhibited at just that electrode separation where the ability of the solution to form a second wave disappears. This apparently indicates a decrease in the energy required for one or both of the electrode processes, or a decrease in the resistance of the solution. For a series of current densities, a family of curves of the same form is produced, each showing this behavior (Figure XII).

As the diffusion layers coalesce at still smaller electrode separations, there is a further decrease in the voltage required to produce a given current density.

In all regions of electrode separation, current density remains stable with time, which indicates a nearly equal electrode efficiency at both anode and cathode; otherwise, a concentration change would quickly manifest itself through a change in the conductance of the solution, as well as in the spacing of the general fringe pattern.

FIGURE XII

THE EFFECT OF ELECTRODE SEPARATION ON VOLTAGE PRODUCING A CONSTANT CURRENT DENSITY



PART V. Solutions other than $CuSO_4$

It is here felt desirable to do some study on solutions other than $CuSO_4$, particularly since all the published work of O'Brien and Ibl have dealt with this solution. Samarcev[4] obtained an interference pattern for $ZnSO_4$ similar to that shown in his work with $CuSO_4$, and calculated diffusion constants for Zn^{++}. His electrodes were arranged horizontally, but this did not seem to bring about any large differences from the vertical arrangement used by Ibl, O'Brien, and in the present work.

Another study, also with the electrodes in a horizontal position, has been made of a flow system using a Cd anode, $CdSO_4$ as the electrolyte, and a silver cathode coated with mercury[5]. A fringe pattern qualitatively similar to the one described was found; the work could not be quite comparable as the electrodes were placed in the top and bottom of a pipe, and the electrolyte flowed through the system at a rate of between 15 and 45 cm/second. The authors, C.S. Lin, R.W. Moulton, and G.L. Putnam, recognized the fringe shift they found as a concentration gradient, but they did not compute any absolute values or give the dimensions of their cell with sufficient accuracy to permit

---

[4] A.G. Samarcev, Zhur. Fiz. Khim., 10, 1424-8 (1934)

[5] C.S. Lin, R.W. Moulton, G.L. Putnam, Ind. and Eng. Chem., 45, 636 (1953)

such a calculation to be made from their data. The photograph which they have published gives no indication of the formation of a second wave.

The alternate electrolytes selected for a study here were $AgClO_4$ (between Ag electrodes) and $NiSO_4$ (between Ni electrodes).

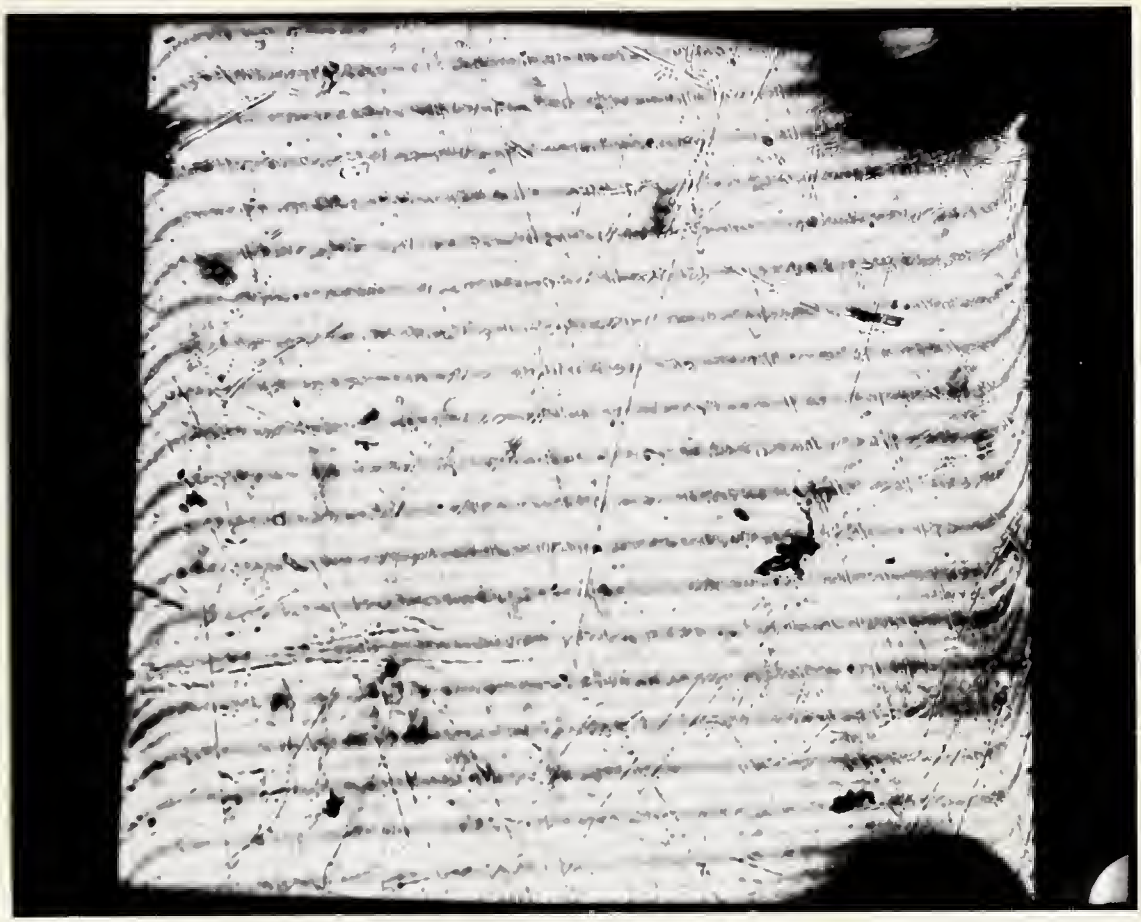
The solution of $AgClO_4$ was prepared by heating $AgNO_3$ with a large excess of 72% perchloric acid on a hot plate in a fume hood until copious fumes of $HClO_4$ were evolved. The mixture of crystals was then dried at 150° in a vacuum, and next dissolved in distilled water without further purification. The principal impurity would be $HClO_4$, which was not removed because its presence decreases the rate at which the solution decomposes upon exposure to light. Two solutions were prepared, one .015 M, having a pH of 3.2 and the other .12 M, having a pH of 2.9.

Since blocks of silver for use as electrodes were not available, electrodes were made by cutting strips of silver foil, which formed the surface on which deposition occurred, and from which silver ions were produced in the electrode process. The strip was placed in a mold, and extended around to the rear of the mold, and up out of the mold. The interior was filled with Araldite, hardened in a 70°C. oven, and filed to the proper size.

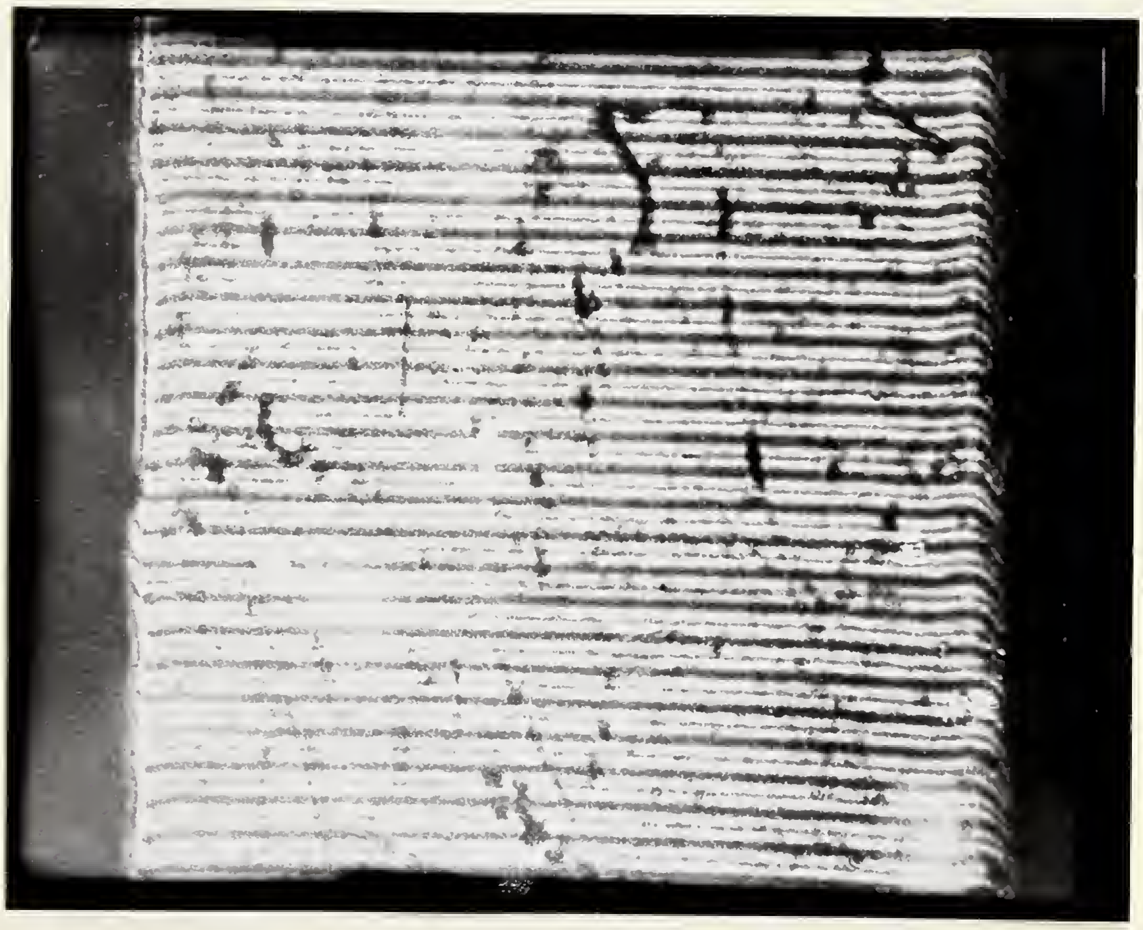
The solution of .015 M $AgClO_4$ showed no second wave up to a voltage of 1.5 volts, or 1500 micro-amperes/cm^2. However, at this current density the $CuSO_4$ solution occasionally does not show a second wave clearly, so the more concentrated solution was investigated. At moderately low current densities (around 5 milliamperes/cm^2) a second wave was first noted, but before it could be photographed, it disappeared, although the current density did not change. At a current density of 100 milliamperes/cm^2 a second wave about 1/4 fringe in magnitude was formed, which remained until the finely powdered silver being formed at the cathode rendered the solution opaque.

A $NiSO_4$ solution was studied in concentrations of 33 grams $NiSO_4 \cdot 5H_2O$ per liter, and 1 gram per liter. In both cases no second wave was observed, although the current density was increased until the evolution of hydrogen began. One of these photographs is shown on page 77, along with a $CuSO_4$ interferogram for comparison. Interferograms were obtained from the electrodeposition of the 33 grams per liter solution at .4 milliamperes/cm^2 and 3 milliamperes/cm^2. In the latter, hydrogen was already being evolved, but the photograph was obtained nevertheless. The voltage was thereafter increased to 3 volts; the velocity of evolution of hydrogen increased, but no second wave formed. These results were obtained quickly after the current was

$NiSO_4$ - $CuSO_4$ COMPARISON



$NiSO_4$, 3 mA/cm^2, 33 grams/liter, 30°



$CuSO_4$, 2 mA/cm^{2}30 grams/liter, 30°

turned on, before passivity became appreciable. The tendency of the nickel electrodes to become passive was noted shortly thereafter.

One drop of a 1% gelatin solution was added to 10 milliliters of the 30 gram/liter $CuSO_4$ solution, and a run performed on some of this $CuSO_4$. Although this gelatin solution is very useful in suppressing the maximum in a polarographic curve, it had no effect on the system of interference fringes. The only difference observed due to this additive was the retardation of the evolution of hydrogen.

CHAPTER IV

INTERPRETATION: FIRST WAVE

It has previously been recognized both by Samarcev[1] and by O'Brien[2] that the first wave may be interpreted as a change in the concentration of the solution, and that the magnitude of that concentration change can be calculated quantitatively. The expression to be used is

$$m\lambda = \Delta n \; d \cos \theta \qquad (4,1)$$

in which m is the number of wavelengths of displacement in the interference fringe pattern, λ is the wavelength of the light, Δn is the change in refractive index, d is the difference in distance travelled by two interfering beams, and θ is the angle between the reflected beam and the perpendicular to the surface of the flats.

The electrodes are 1.92 millimeters in thickness, as measured by a vernier caliper; the difference in distance travelled by two interfering beams is twice this, when θ is almost exactly 0, or 3.84 millimeters (3.84×10^7 A°). Since the wavelength of the sodium D line is 5893 A°, the path difference between the two interfering beams would be be 6.52×10^3 wavelengths, so for a one-fringe displacement,

---

[1] A.G. Samarcev, Z. Physik. Chem., A168, 45, (1934)

[2] R.N. O'Brien and H.N. Axon, Trans. Inst. Metal Finishing, 34, 41-52 (1957)

Δn would be .000153. The data obtained with the differential refractometer[3] showed that 1 gram/liter change in $CuSO_4$ concentration produced a change of .000137 in index of refraction. Dividing, we obtain 1.12 gram/liter/λ; that is, one fringe displacement indicates a concentration change of 1.12 gram per liter in the concentration of $CuSO_4$ in the solution. The dependance of this figure on concentration is less than 2% and will be neglected.

Samarcev used Fick's law of diffusion directly to calculate the diffusion constant for $CuSO_4$; however, Fick's law is basically empirical, and does not allow for the contribution of the applied potential to the diffusion rate. According to Keulegan[4] we may represent the total concentration gradient developed in a solution in the presence of an applied potential by the expression:

$$\frac{\partial n_j}{\partial t} = A\,D_j \frac{\partial c_j}{\partial y} + A\,U_j c_j z_j e \frac{\partial V}{\partial y} \qquad (4,2)$$

in which $\partial n_j / \partial t$ represents the number of ions of the jth kind passing across a cross-section per second; A is the cross-sectional area; D_j is the Fick diffusion constant of the jth ion; c_j is its concentration, U_j its mobility, and z_j its valence; V is the applied potential, and y the

---

[3] M.R. Chakrabarty, unpublished results

[4] G.H. Keulegan, J. Research Nat. Bureau of Standards, 47, 156 (1951)

distance perpendicular to the electrode.

Since for an ideal solution $D_j = U_j kT$ [5] in which k is the Boltzmann constant and T is the absolute temperature,

$$\frac{\partial n_j}{\partial t} = A\,D_j \frac{\partial c_j}{\partial y} + \frac{A\,c_j D_j z_j e}{kT}\,\frac{\partial v}{\partial y} \qquad (4,3)$$

If we let f_j be the number of ions reacting per Faraday of current passing, then at the electrode-electrolyte interface (y=0):

$$\frac{\partial n_j}{\partial t} = \frac{f_i\ I}{F}$$

Thus:

$$\frac{f_j I}{F} = AD_j\left(\frac{\partial c_j}{\partial y}\right)_{y=0} + \frac{AC_j}{kT}\ z_j\ e\left(\frac{\partial V}{\partial y}\right)_{y=0} \qquad (4,4)$$

Multiplying (4,4) through by the factor z_j/D_j, we obtain:

$$\frac{f_j I z_j}{FD_j} = Az_j\left(\frac{\partial c_j}{\partial y}\right)_{y=0} + \frac{Ac_j}{kT}\ z_j^{\,2} e\left(\frac{\partial V}{\partial y}\right)_{y=0} \qquad (4,5)$$

for the jth ion. If there are i ions in the solution, a similar equation may be written for each of them. Summing all such equations, we obtain:

$$\frac{I}{F}\sum \frac{f_i z_i}{D_i} = A\sum z_i\left(\frac{\partial c_i}{\partial y}\right)_{y=0} + \frac{Ae}{kT}\left(\frac{\partial V}{\partial y}\right)_{y=0}\sum z_i^{\,2} c_i \qquad (4,5)$$

---

[5] H.S. Harned and B.B. Owen, "The Physical Chemistry of Electrolytic Solutions, 3rd Ed., Reinhold Publishing Corp., New York, (1958), p. 118.

Since there can be no macroscopic separation of charges in the solution, the sum for all ions, $\sum z_i c_i = 0$, and the first term on the right hand side of (4,6) must vanish. Solving the remaining expression for $(\partial V/\partial y)_{y=0}$ the result is obtained:

$$\frac{IkT}{AFe}\frac{\sum z_i f_i/D_i}{\sum z_i^2 c_i} = \left(\frac{\partial V}{\partial y}\right)_{y=0} \qquad (4,7)$$

Substituting (4,7) into (4,4) gives:

$$\left(\frac{\partial c_j}{\partial y}\right)_{y=0} = \frac{I}{AF}\left[\frac{f_j}{D_j} - c_j z_j \frac{\sum f_i z_i/D_i}{\sum z_i^2\, c_i}\right]_{y=0} \qquad (4,8)$$

Now let us consider a solution of $CuSO_4$. The only ions present in appreciable quantities will be Cu^{++} and $SO_4^{=}$. In a solution of concentration a, these relations will hold:

For Cu^{++}:

$$\left(\frac{\partial c_{Cu^{++}}}{\partial y}\right)_{y=0} = \frac{I}{AF}\left[\frac{1/2}{D_{Cu^{++}}} - 2a\, \frac{\sum 1/2 \cdot 2/D_{Cu^{++}} + \frac{0(-2)}{D_{SO_4^{=}}}}{4a+4a}\right]$$

$$= \frac{1}{4}\,\frac{I}{AFD_{Cu^{++}}}$$

where a is the concentration of the solution. For $SO_4^{=}$:

$$\left(\frac{\partial c_{SO_4^{=}}}{\partial y}\right)_{y=0} = \frac{I}{AF}\left[\frac{0}{D_{SO_4^{=}}} + 2a\, \frac{\sum 1/2 \cdot 2/D_{Cu^{++}} + \frac{0(-2)}{D_{SO_4^{=}}}}{4a + 4a}\right]$$

$$= \frac{1}{4}\,\frac{I}{AFD_{Cu^{++}}} \qquad (4,9)$$

Applying this equation (4,9) to the case of a solution of pure $CuSO_4$, in which the only two ions present in any appreciable quantity are Cu^{++} and $SO_4^{=}$, and the reaction at either electrode is the dissolution or deposition of Cu, the experimental data may be used to calculate the diffusion ceofficient for Cu^{++}.

For example, a solution containing 10 grams per liter of $CuSO_4$ is found to show a shift of one fringe at 500 micro-amperes at a temperature of 15°C. The width of the first wave is found to be .110 millimeter, and the region of the first wave is observed to be very nearly linear. (Only the region of the first wave is considered, since the assumption

$$\frac{\partial n_i}{\partial t} = \frac{f_i\ I}{F}$$

is unequivocally true only at the immediate vicinity of the electrode)

$$\frac{.00112/160}{.0110} = \frac{5.00 \times 10^{-4}}{4 \times .48 \times 96{,}489.9\ D_{Cu^{++}}}$$

and therefore

$$D_{Cu^{++}} = .437 \times 10^{-5}\ \text{cm}^2/\text{second.}$$

In this equation, .00112 is the concentration change expressed in grams per cubic centimeter; this is divided by 160, the molecular weight of $CuSO_4$ to obtain Δc in moles per cubic centimeter; .0110 is the width of the first wave

in centimeters (Δy); 5.00×10^{-4} is the current in amperes; .48 is the electrode area in square centimeters; 96,489.9 is the Faraday.

This value of $.437 \times 10^{-5}$ for the diffusion constant of Cu^{++} in cm^2/second may be compared to the literature one of $.45 \times 10^{-5} \pm .05 \times 10^{-5}$ for a .1 N $CuSO_4$ solution at 17°C.

In general, the values obtained by this method tend to be a little higher than those in the literature. This might be due to any or all of three factors. First, the literature values are only given an accuracy of ± 10%; second, our solution would have a concentration of .0626 N, while the literature values are for .1N, and an increase in dilution raises the diffusivity of the solute; third, the comparison values are obtained by permitting a solute to diffuse into a vessel of pure water, so if there were any difference in the rate of movement between Cu^{++} and $SO_4^{=}$, these values for Cu^{++} would not be expected to quite agree with those for the salt as a whole. These values for the cation only should be very useful to polarographers.

Table IX gives the diffusion constants calculated from the experimental data for 10 grams/liter Cu^{++} at a number of temperatures.

It is concluded that the first wave is the diffusion layer.

It is interesting that the width of the first wave so

TABLE IX

Diffusion constants of Cu^{++} in Copper sulphate at various temperatures (cm^2/sec); 10 grams/liter

Temperature	$D_{Cu^{++}}$	Temperature	$D_{Cu^{++}}$
6°(1°)	$.473 \times 10^{-5}$	30°	$.618 \times 10^{-5}$
7.5°(4°)	$.493 \times 10^{-5}$	35°	$.655 \times 10^{-5}$
8.7°(7.8°)	$.418 \times 10^{-5}$	39° (40°)	$.681 \times 10^{-5}$
13.5°	$.433 \times 10^{-5}$	42° (45°)	$.792 \times 10^{-5}$
15°	$.437 \times 10^{-5}$	46° (50°)	$.927 \times 10^{-5}$
27.7°	$.537 \times 10^{-5}$	50° (55°)	1.17×10^{-5}

Comparison values[6]

$.40 \times 10^{-5}$	10°
$.45 \times 10^{-5}$	17°
$.50 \times 10^{-5}$	20°

---

[6] International Critical Tables, 1st Ed., McGraw-Hill Book Co., Volume V, p.65 (1929)

adjusts itself as to give a constant diffusion constant, although the relationship between current density and the magnitude of the fringe shift is not a linear one.

In making these measurements, the anode data is, and has been throughout this investigation, relied upon almost exclusively. A multiple beam apparatus is not adapted to the measurement of fringe displacements about the cathode, particularly when the concentration gradient becomes appreciable. The fringes fall upon one another and can not be resolved.

As a result of this effect, in determining the layer-thickness for determination of diffusion constants, it is necessary to measure both the cathode and anode layers and average the two values, to correct for refraction.

The plane of focus of the fringes also changes with the concentration changes, so it is not possible to have the microscope exactly focused on both anode and cathode simultaneously.

A plot of $\log D_{Cu^{++}}$ versus 1/T yields an activation energy for diffusion of about 4 kilocalories/mole, varying slightly as to whether or not correction for varying viscosity and density is made. The 6° (1°) and 7.5° (4°) points do not lie on the linear portion of the plot.

CHAPTER V

INTERPRETATION: SECOND WAVE

The second part of the interference pattern, first reported by Ibl[1] but simultaneously observed by O'Brien[2], who called it the second wave, is observed as a gradient in the refractive index in a direction opposite to that observed in the diffusion layer. Ibl investigated the possibility that the phenomenon might be attributed to an optical effect by using electrodes of several thicknesses, in the same manner as in this work. Ibl also found that the second wave was directly proportional to the thickness of the electrodes, at constant current density, which means that the change in refractive index remains the same at the same current density. Ibl therefore concluded that the effect was not an optical or surface phenomenon.

Ibl next considered the possibility that the second wave might be a result of a change in temperature in the region of the electrodes. To test this possibility, two series of experiments were performed; in the first, large copper blocks served as electrodes; inthe second, thin strips of copper foil were substituted. The two pairs of

---

[1] N. Ibl and R. Müller, Z. Elektrochem., 59, 671-6, (1955)

[2] R.N. O'Brien and H.J. Axon, Trans. Inst. Metal Finishing, 34, 41-52 (1957)

electrodes would differ markedly in their ability to carry away any heat liberated by the reactions occuring in solution, but no difference in the fringe pattern was observed. Ibl concluded that the second wave could not be caused by temperature gradients in the solution. The recent work of Holmes and Joncich[3] dealt with the measurement of the temperatures of the electrodes and solutions at various current densities; the temperature gradients are found to be of the order of a few tenths of a degree at current densities considerably larger than discussed in either this work or that of Ibl. This confirms Ibl's conclusion that the observed second wave could not be due to a temperature gradient. A second wave shift of one fringe would represent about a 1° temperature change, which would require a current density more than ten times as large as any discussed here.

Ibl also notices no significant differences between solutions of different concentrations.

From these observations, Ibl conclusded that the second wave might represent an actual concentration gradient. He felt the phenomenon might be caused by natural convection, and that it might be detected by other than interferometric means. He added collophonium to his $CuSO_4$ solution and obtained very remarkable photographs showing clearly the

---

[3] H.F. Holmes and M.M. Joncich, Anal. Chem., 31, 29-32, (1959)

paths of individual collophonium particles in the solution, and neatly outlining the convection pattern. His equation expressing the relationship between convection velocity and the height of the cell was given in Chapter 1. (Equation 1,1) This equation showed that the velocity of motion of the bulk of the solution at the region of greatest turbulence was proportional to the 3/5 power of the height of the cell and to the 2/5 power of the current density. His data showed that, for example, at a current density of 3 milliamperes per square centimeter, in a cell 70 millimeters in height, the maximum convective velocity would be about 1.3 millimeters per second.

Let us see what the velocity maximum present in a cell only 2 millimeters in height should be: $(70)^{3/5} = 12.8$; $(2)^{3/5} = 1.53$; therefore, the maximum convective flow, v, at the same current density between 2 millimeter electrodes should be in proportion to these 3/5 powers:

$$\frac{v}{1.53} = \frac{1.3}{12.8} \qquad (5,1)$$

$$v = .155 \text{ millimeters per second}$$

The velocity of material transport in our system under the force of the applied voltage would be calculated in this manner: since the cell is about 2 millimeters x 2.5 centimeters x 3 millimeters, its volume is .15 cc. A solution of 10 grams $CuSO_4$/liter will contain .00057 grams of copper in .15 cc. The equivalent weight of copper being 31.76 grams,

this solution will contain 1.8 x 10^{-5} equivalents of copper. A current density of 3 milliamperes/cm^2 would be about 3 x 10^{-8} equivalents of copper being deposited per second. Since the solution contains about 1.8 x 10^{-5} equivalents, an ion would be in the solution when this current is being passed an average of 6 x 10^2 seconds. In this period of time, it travels 3 millimeters, so its average velocity would be about 5.98 x 10^{-3} millimeters per second. The maximum theoretical convective velocity in this solution as calculated from Ibl's fomula would indeed be some two orders of magnitude larger than the transport velocity in a cell of this size.

Although it would seem that Ibl's interpretation of the second wave might be valid if his formula holds, it is very difficult to interpret what changes might be caused by possible differences in his parameters λ, ω, ϕ and η. Ibl gave no means of calculating these parameters, so we cannot evaluate their physical significance. It would seem from the convection patterns that he has published, that an appreciable mixing of the more concentrated solution from the anode side would occur before the solution were transported to the region of the cathode, and that a similar mixing would occur before the other flow reached the anode. If the second wave is caused by a convection mechanism, there

should be a region at each of the non-conducting ends of our cell, in accordance with Ibl's equation (1,3) in which the second wave does not appear. This is not observed. It is very difficult to envisage a large amount of convection occuring in three drops of liquid not subject to any processes with large heat effects. Further, the first run with the saturated solution, in this work, performed before the solution was filtered, contained many minute, microscopic crystals of $CuSO_4$. If there had been the calculated amount of turbulence in the solution, they should have moved with the convective flow and revealed its presence, as in Ibl's collophonium experiments; but the minute crystals photographed sharply and remained in exactly the same position throughout the run. Although the fringe shifts could not be measured in that run, because of the presence of so many crystals, and the results had to be discarded, the run did show that a large amount of any stirring effect could not have been present in the solution.

Ibl's cells ranged between 7 and 11 centimeters in height; the volumes were in the range of about 100 milliliters. Although his calculated and observed data agreed nicely in the range in which he worked, it would appear that it may not extrapolate accurately to cells of the depth and volume used here. Should the Ibl theory be correct, some variation in the expected maximum velocity and therefore in the

refractive index change in the second wave would be expected; but Ibl himself found no lack of proportionality between either wave and the thickness of the solution. Ibl's theory totally fails to explain the disappearance of the second wave in $NiSO_4$ (see page 77); if the anodic diffusion layer in $CuSO_4$ can diffuse over to the region around the cathode, it should do the same thing in any other salt, and the extent should be regulated only by the viscosity of the medium and the diffusion constant (because this controls the magnitude of the concentration gradient forming the diffusion layer).

A personal correspondence from Brenner (whose samples turned off on the lathe gave a curve of concentration versus distance from the electrode, but did not show any maximum or minimum in concentration except at the electrode) states that he feels his work would have detected an increase in concentration amounting to 10% of the concentration polarization in the diffusion layer, and that his data gave no indication of such an occurance.

O'Brien[4] measured the decay time for both first and second waves; the second wave disappeares in about a second after the current is turned off, but the first wave requires about a minute. These measurements are subject to

---

[4] R.N. O'Brien, thesis, op. cit. (1955)

considerable error, and O'Brien is at present improving them by obtaining motion pictures of the formation and decay of the fringe pattern. These facts also suggest that the second wave might well not be a concentration gradient. No calculations will be made, but since the second wave disappears about 60 times as fast as the first, and has a magnitude of 10% of the first wave, one would have to postulate another diffusion constant for this region of the electrode about 6 times as large as the one found.

Summarizing the previously published results on the second wave, it has been observed by two previous workers that a reversal in refractive index gradient takes place at a distance of approximately .15 millimeter from the electrode, and although a mathematically satisfactory convection mechanism has been suggested assuming that this is a concentration gradient, there are quite a number of factors suggesting that this is not the case.

The refractive index of a solution may depend on these factors: the concentration of the solution, the temperature, the wave length of the incident light, the nature of the solute, the nature of the solvent, and the forces between these species.

In the case in question, the incident light is always the sodium D line, the wavelengths of which are constant. The temperature effects are known to be too small to be

more than a very minor portion of the effect. The solute is $CuSO_4$, the solvent water. If we are to accept the evidence of Brenner and O'Brien that no concentration maxima or minima occur in this region, only the last possibility remains.

It would at first seem possible that a rearrangement in the orientation of solvent molecules about a copper ion might occur, giving rise to a change in the specific index of refraction without requiring any change in concentration. In the course of electrodeposition at, for example, the cathode, an ion-pair must approach the electrode, lose a part of its solvation (eventually, all of it); the ion pair must dissociate--perhaps, as Bockris believes, the cation is adsorbed onto the electrode, where it moves along the surface of the electrode to a position where a dislocation in the metal crystal lattice occurs. It must then accept two electrons, and become a part of the cathode. At the anode, the reverse process must occur. Either a change in the extent of hydration or the extent of ion-pair formation could conceivably account for the observed second wave. $CuSO_4$ in solution is quite strongly hydrated, as evidenced by the entropy change of 46.6 e.u.[5], but it also forms ion-pairs, the cryoscopically measured equilibrium constant

---

[5] Handbook of chemistry and physics, 36th Ed., 1954, p. 1718

for the dissociation being .0035 at 25°C.[6]

Let us see in which direction each of these two possible effects might be expected to act. While quantitative correlations showing on which properties the refractive index of a compound depends have not been agreed upon*, it is reasonable in the opinion of this author to assume that the effect of a material on light might be similar to its effect on x-rays--another form of electromagnetic radiation. Since the thickness of a solid absorbant needed to reduce the intensity of radiation from a x-ray source by 1/2 is an inverse function of the atomic number of the absorbant, it would seem that the ability of matter to slow down the passage of electromagnetic radiation is a direct function either of the charge on the nucleus or of the electron density.

In is in accordance with this line of thinking and the general consensus of opinion that the greater the density, the higher the refractive index. Hence, lead glass has both an exceptionally high ability for the absorbing of gamma rays--hence its extensive use in connection with master slaves and the handling of high levels of radiation.

---

[6] R.A. Stokes and R.H. Robinson, "Electrolyte Solutions", Second Ed., Butterworth Scientific Publications (1959) p. 414.

* Opposite points of view are given by C.J.F. Boettcher, "Theory of Electic Polarization", Elsevier Publishing Co., Houston, pp. 273-81 (1952) and K. Fajans, "Chemical Forces and Optical Properties of Substances, McGraw-Hill Book Co., New York, (1931)

When water freezes, producing the more open-structured ice, the refractive index is decreased. Again, when it expands with increasing temperature in the liquid state, the refractive index decreases. When $CuSO_4$ is added to water, the partial molar volumes of both are diminished, as the hydration of the $CuSO_4$ causes a tighter, closer packing of the water molecules. It is to be expected therefore, that any disruption of the hydration of Cu^{++} ions at a cathode could bring about a decrease in refractive index quite independant of any concentration change. The effect would probably be small, but it would be in the wrong direction to account for the observed second wave, a cathodic maximum. It could conceivably account for the third wave, but the shape of the curve in $NiSO_4$, where no second wave was present, suggests that the third wave may be merely a backward extension of the first wave. Again considering the $Ni\ SO_4$, while it is difficult to guess just what effects occur in various ions in secondary hydration sheaths, it would be rather surprising if nickel and copper were strikingly different in this respect, and thus, the complete absence of a second wave in $NiSO_4$ gives another indication that this hydration-change explanation is not the correct one, although [illegible] is the next fairly obvious mechanism to present itself.

The pH of the solution is known to increase at the

cathode and decrease at the anode, but this change would occur in any solution, including $NiSO_4$. This change would be in the correct direction, and acts over a large enough range,[7] but is a smaller effect in its contribution to the refractive index (assuming a pH change from 4 to 10 at the cathode, and of the same order of magnitude at the anode) than ion pair effects. At high voltages, this effect could become important or even dominant, and probably accounts for the second wave observed in Ag ClO_4. The ensuing discussion will be useful for further consideration of this possible effect.

The remaining possible explanation deals with the possibility that the formation and dissociation of ion-pairs at the elctrodes might account for the second wave. Here this striking difference between copper and nickel may be explained. The striking fact lies in the apparent spectrally-observed association properties of $NiSO_4$. Duncan and Keppert[8] have recently found that the association of $NiSO_4$ appears to be extremely tenuous; the Ni^{++} ion is apparently so firmly hydrated that the $SO_4^{=}$ ion cannot easily approach. According to their interpretation[8], there must

---

[7] M.N. Polukarpov, J. Gen. Chem., U.S.S.R., 19, a1-a28, (1949)

[8] J.F. Duncan and D.L. Keppert, in "The Structure of Electrolytic Solutions, ed. by Hamer, John Wiley and Sons, New York, (1959), p. 398

be always a separation of more than one water molecule between Ni^{++} and $SO_4^{=}$; there is no detectable spectral evidence of ion pair formation in $NiSO_4$ at all, although cryoscopic and conductimetric evidence indicates that $NiSO_4$ is quite extensively associated. Either $NiSO_4$ is associated at a distance, as Duncan and Keppert suggest, or else for some unknown reason the association is not detected spectroscopically. For $CuSO_4$, on the other hand, spectral evidence of ion-pair formation is well established. Thus, as far as electronic transitions affecting the passage of light are concerned, $NiSO_4$ appears unassociated in solution, despite its cryoscopic behavior to the contrary. It is the effect of the passage of light on the solution with which we are concerned in a study of the refractive index. The dissociation constant of $CuSO_4$, spectrally obtained by Bale, Davies, and Monk[9] is .0047 ± .0002 at 25°C. The fact that this is slightly larger than the cryoscopic dissociation constant may indicate some small degree of water present between Cu^{++} and $SO_4^{=}$ in an ion pair, but the difference from $NiSO_4$ is most striking. By use of the formula $\Delta F° = -RT\ln K$, we may calculate $\Delta F°$ for the dissociation of $CuSO_4$ ion pairs, 3.2 kilocalories per mole.

Since $\Delta F° = -nFE°$, the potential associated with the dissociation of the ion-pairs would be 3.2 kilocalories

---

[9] W.D. Bale, E.W. Davies, and C.B. Monk, Trans. Faraday Soc., 53, 816-23 (1956)

per mole, x 4.18605 joules/coulomb x 1 mole/2 equivalents x 1 equivalent/96,489.9 coulombs; E° = -.068 volts.

At the separation of the electrodes where the capability of the solution to form the second wave vanished (between separations of .65 and .70 millimeters) the voltage required to produce the same current density decreased by .01 to .02 volts; since the process of formation of the ion pairs should be at least partially reversible, the observed change should be (and is) somewhat smaller than the calculated one, but they are certainly of the same order of magnitude, and it is possible that at this electrode separation the solution no longer forms ion pairs in sufficient numbers to require this voltage.*

Quite a body of information concerning the specific refractive indices of various associated and dissociated ions appeared in Zeitschrift für Physikalische Chemie in the late 1920's and early 1930's, which has since been largely neglected. Associated and dissociated forms of the salts were found to have different molar refractive indices, and this gives us a tool for comparison, permitting calculation of the extent of ion-pair formation and dissociation being observed in the region of the second wave.

Molar refraction was defined by Meyer and Heck[10] as:

---

[10] G. Meyer and A. Heck, Z. Physik. Chem., 100, 316-33 (1922)

* Highly speculative. See appendix.

$$R = \frac{n^2 - 1}{n^2 + 2} \quad \frac{M}{d} \qquad (5,2)$$

in which R is the molar refraction, n is the refractive index, M is the molecular (or ionic) weight, and d is the density, in grams/cc. This quantity (R) is independant of temperature.

For mixed electrolytes, either containing several ions or associated and dissociated forms of the same ions, Geffchen[11] developed:

$$R_{sp} = \frac{p_1R_1 + p_2R_2 + \ldots\ldots}{p_1 + p_2 + \ldots\ldots} \qquad (5,3)$$

where each p_i represents a concentration and each R_i the molar refractive index of a species present in the solution.

Luhdemann[12] then obtained R for a number of salts, and Fajans and Luhdemann[13] calculated the ionic refractions for the completely dissociated ions. Some of their data are presented in Table X. The molar refractions for the salts were determined more accurately than listed in Table X; the molar refraction decreases with decreasing concentration. The four digit values shown in Table X are average values. The sum of ionic refractions, when appreciably different

---

[11] W. Geffchen, Z. Physik. Chem., B25, 460-70 (1934)

[12] R. Luhdemann, Z. Physik. Chem., B29, 133-49 (1935)

[13] K. Fajans and R. Luhdemann, Z. Physik. Chem., B29, 150-7 (1935)

TABLE X

Molar refractions as determined by Luhdemann. (Digits beyond the region of agreement have been dropped)

Salt	R	Salt	R
1/2 $CdCl_2$	10.26	HIO_3	19.29
1/2 Na_2SO_4	7.58	$LiIO_3$	19.19
HI	18.55	HNO_3	10.32
NH_4NO_3	15.27	HCOOH	8.55
NaCOOH	10.07		

More molecular refractions, determined by Geffchen and Price[14]

Salt	R	Salt	R
NaBr	12.82	$1/2(NH_4)_2SO_4$	7.56
KCl	11.30	$1/2\ (NH_4)_2CO_3$	6.27

Ionic refractions as calculated by Fajans and Luhdemann

Ion	R	Ion	R
H^+	-.52	OH^-	5.15
Li^+	-.32	NO_3^-	11.01
Na^+	.20	IO_3^-	19.45
K^+	2.25	ClO_4^-	13.24
Rb^+	3.79	$HCOO^-$	9.88
Cs^+	6.53	1/2 $CO_3^=$	6.07
NH_4^+	4.315	1/2 $SO_4^=$	7.36
1/2 Ca^{++}	.355	F^-	2.60

TABLE X, cont.

1/2 Sr^{++}	.945	Cl^-	5.15
1/2 Zn^{++}	.305	I^-	19.22
1/2 Cd^{++}	1.16	Br^-	12.66

---

[14] W. Geffchen and D. Price, Z. Physik. Chem., B26, 81-99 (1934)

the molar refraction of the salt, are invariably greater. The formation of the ion pair, if it brings about an electronic interaction between the ions, decreases the effect of the electrons on the incident light, thus decreasing the molar refraction of the pair.

Calculation of the specific molar refractive index of Cu^{++} is made in the following manner:

Concentration (grams $CuSO_4$/liter)	Refractive index*	Density*	1/2R
6.49	1.33353	1.0063	16.386
12.82	1.33471	1.0125	16.286
18.78	1.33571	1.0185	16.226
25.91	1.33692	1.0251	15.819

The first three points plot quite linearly; beyond this, the R decreases more rapidly. Extrapolating to infinite dilution yields 16.45 as the 1/2 R for $CuSO_4$. From Fajans' calculations, 1/2R for $SO_4^{=}$ is 7.36, so 1/2 R for Cu^{++} would be 9.09. The change produced in the refractive index in the case of a solution containing 10 grams $CuSO_4$ per liter if the ion pairs present dissociated would thus be 7 parts in 1639, or about 1 part in 235. The maximum change this could produce in the refractive index of the solution would be that associated with the dissociation of all of the

---

* Unpublished results of M.R. Chakrabarty, this laboratory, 22°C.

** Interpolated from Handbook of Chemistry and Physics, 36th Ed., p. 1829.

ion pairs existing in that solution; an increase in R of .426%, which would affect n by:

Differentiating (5,2), we obtain:

$$\frac{dR}{dn} = \frac{M}{d} \frac{(n^2 +2)\ 2n - (n^2-1)\ 2n}{n^4 +4n^2 + 2} \qquad (5,4)$$

$$\frac{dR}{dn} = \frac{M}{d} \quad \frac{2n}{n^4 +2n^2 +4}$$

At 6.49 grams $CuSO_4$ per liter, n is 1.33353, d is 1.0063, M is 159.61, so:

$$\frac{dR}{dn} = \frac{159.61}{1.0063} \quad \frac{2.66706}{31.6235 + 3.55660 + 4} = 11.69215$$

$$.426\% = 11.69215\ \Delta n$$

$$\Delta n = .0364\%$$

n = 1.33353 so Δn is .00048.

This change in refractive index would give a fringe shift of 3.042 wave lengths of Na_D with 2 millimeter electrodes in a 10 gram per liter $CuSO_4$ solution, and the dissociation at the cathode would be an increase in refractive index, the observed phenomenon. In a solution of this concentration, this calculated maximum possible effect is ample to account for all observed increases in index of refraction, the largest observed by O'Brien being about 1 fringe shift, in plain $CuSO_4$ solutions.

At the anode, a minimum in refractive index is observed. This cannot be accounted for by a dissociation of ion-pairs; it therefore becomes necessary to postulate

that sufficient $SO_4^=$ adions are present, which unite with Cu^{++} ions being discharged from the anode forming a greater-than-normal number of ion-pairs, or perhaps, some higher complexes. From the dissociation constant of .0047 and the mass action law, it is found that in a solution containing 10 grams/liter (.0626 N), 45.58% of the $CuSO_4$ should be paired at equilibrium under the influence of no external forces; hence, producing a minimum by forming additional pairs, or possibly higher complexes, would be quite feasable.

At very low current densities, the ions are able to diffuse to within a few angstroms of the electrode before dissociating, but as the voltage is increased, enough potential gradient must develop in the region of the second wave to cause an increasing portion of the ion-pairs to dissociate in this region. It might therefore be postulated that a sharp potential gradient should be located here; unfortunately, the contours of the potential gradient have not as yet been established.

The possible effect of pH changes could be calculated as follows; assuming that the cathodic pH would change from about 4 to 10, as observed by Polukarpov[15] and assuming electroneutrality, the concentrations of ions present would

---

[15] M.N. Polukarpov, J. Gen Chem., U.S.S.R., 19, a1-a28, (1949)

change through the addition of $10^{-4}N$ OH^-. So that there be no separation of charges, $10^{-4}N$ $SO_4^=$ must leave. $10^{-4}N$ H^+ would leave and $10^{-4}N$ Cu^{++} enter. Using Fajans' ionic molar refractions and the Cu^{++} value just calculated, the molar refraction change would be:

$$10^{-4}(5.15 - 7.36 + .52 + 9.09) = 8.4 \times 10^{-4}$$

Rsp according to equation (5,3) would be 16.39:

$$\frac{.0626\ (16.38) + 10^{-4}(8.4)}{.0626} = 16.39$$

The increment brought about at the cathode could be as great as about 1/6 of that observed due to ion-pair dissociation at the cathode, but increased voltages do not increase the pH appreciably beyond 10, due to the formation of colloidal $Cu(OH)_2$ [15]. The change at the anode, assuming a pH change equal to that at the cathode, from a H^+ concentration of about 10^{-4} to 2×10^{-4}, could be

$$10^{-4}(-.52 - 9.09) = -9.61 \times 10^{-4}$$

If this pH change occurs, the effect on R_{sp} would be:

$$\frac{.0626(16.38) + 10^{-4}(9.61)}{.0626} = 16.40$$

Again, this increment would only be about 1/6 as great as the effect of dissociation of the ion pairs. The effect undoubtedly contributes to the second wave, but cannot produce all of it.

---

[15] M.N. Polukarpov, op. cit.

It should be pointed out that the pH of 10 observed at the cathode by Polukarpov was at a voltage of .9 - 1.1 volts; most of our solutions used a considerably smaller voltage, and would probably give a pH effect smaller than calculated by perhaps a factor of 3 or 4.

The calculation just made of the pH effect is valid only for $CuSO_4$; a similar calculation for $NiSO_4$ would require the unavailable molar refractive index of Ni^{++}, which could be quite different from that for Cu^{++}.

In solutions chelated by any complexing agent with a refractive index greater than that of the solution as a whole, another possible mechanism for the development of a second wave arised from the flow of the stream of free liberated complexing agent back from the cathode, and from the association of excess free metal ions with the free complexing agent at the anode. In such a case, pH changes brought about by the complexing agent would also have to be considered.

The particular measurements which would be most useful for further work along the lines of this investigation would be;

First, a study of the local pH, probably by the use of a glass micro-electrode, in the region about .1 millimeter from either electrode, but particularly about the anode.

Second, a study of thepotential contour between

the two electrodes, again, possibly with the use of a microelectrode, and again with special emphasis on the region between .1 and .2 millimeters from either working electrode.

Finally, extensive data on the specific molar refractive index of $NiSO_4$. Since $NiSO_4$ forms no second wave, a high molar refractive index for Ni^{++} would rule out a pH change mechanism.

Interferometric studies of other solutions would be useful, but only in the light of data on the specific refractive indices.

CHAPTER VI

SUMMARY

The electrolysis of cupric sulphate has been extensively studied by the use of an interferometric method. A two-wave pattern was found. The first wave was studied with regard to its variations with temperature and electrode separation, and the lack of appreciable variation with concentration (at a low temperature), the thickness of the electrodes, the optical arrangement, and the reflectivity of the glass optical flats noted. Exponential expressions were obtained to adequately express the dependance of the first wave on current density at several temperatures. The first wave was found to be the diffusion layer, and cationic diffusion constants were reproducibly calculated.

The second wave was observed, and several possible explanations for its existence considered. The convection mechanism, and also a possible mechanism based on changes in the hydration arrangement inthis region were discarded altogether. The dissociation of ion-pairs was found to provide a satisfactory mechanism, if the possibility be admitted that $SO_4^=$ adions might cause a greater-than-normal quantity of pairing in the vicinity of the anode. A pH-change mechanism was considered and found potentially possible, although less satisfactory than the ion-pair

dissociation mechanism. To distinguish between the two more conclusively is left to the future.

It is felt that the purpose of providing a better understanding of the electrodeposition process has been accomplished.

BIBLIOGRAPHY

1. Bale, W.D., Davies, E.W., and Monk, C.B., Trans. Faraday Soc., 53, 816-23 (1956)
2. Bockris, J. O'M., and Mehl, W., Can. J. Chem., 37, 199 (1959)
3. Boettcher, C.F., "Theory of Electric Polarization, Elsevier Publishing Co., Houston, pp. 273-81 (1952)
4. Brenner, A., Proceedings of the 29th Annual Convention of the American Electroplater's Society, p. 28 (1941)
5. Chakrabarty, M.R., unpublished results
6. Craig, D.N. and Hamer, W.J., J. Chem. Ed., 37, 258 (1960)
7. Dundan, J.F., and Keppert, D.L., in "The Structure of Electrolytic Solutions", ed. by Hamer, John Wiley and Sons, New York (1959) p. 398
8. Fajans, K., "Chemical Forces and Optical Properties of Substances, McGraw-Hill Book Co., New York (1931)
9. Fajans, K., and Luhdemann, R.Z., Z. Physik. Chem., B29
10. Fick, A., Pogg. Ann., 94, 59 (1885)
11. Geffchen, W., Z. Physik. Chem., B25, 460-70 (1934)
12. Geffchen, W., and Price, D., Z. Physik.,Chem., B26, 81-99 (1934)
13. Handbook of Chemistry and Physics, 36th Ed., 1954, p. 1718
14. Ibid., p. 1829
15. Ibids, p. 3021
16. Harned, H.S., and Owen, B.B., "The Physical Chemistry

of Electrolytic Solutions", 3rd Edition, The Reinhold Publishing Corp., New York, (1958) p. 118

17. Holmes, H.F., and Joncich, M.M., Anal. Chem., 31, 29-32 (1959)

18. Ibl, N., and Müller, R., Z. Elektrochem., 59, 671-6 (1955)

19. Ibl, N., and Müller, R., J. Electrochem. Socl, 105, 346-53 (1958)

20. International Critical Tables, Ist Ed., McGraw-Hill Book Co., 1929, Volume V, p. 65.

21. Keulegan, G.H., J. Research Nat. Bur. Standards, 47, 156 (1951)

22. Kurtz, L. Yu., and Samarcev, A.G., Zhur. Fiz. Khim., 10, 1424-8 (1934)

23. Landolt-Börnstien, Physikalische-Chemischen Tabellen, p. 1042

24. Lin, C.S., Moulton, R.W., and Putnam, G.L., Ind.and Eng. Chem., 45, 636 (1953)

25. Luhdemann, R., Z. Physik. Chem., B29, 133-49 (1935)

26. Meyer, G., and Heck, A., Z. Physik. Chem., 100, 316-33 (1922)

27. Nernst, W., Z. Physik. Chem., 2, 613 (1888)

28. O'Brien, R.N., thesis "An Optical Study of Electrodeposition," University of Manchester, 1955

29. O'Brien, R.N., and Axon, H.J., Trans. Inst. Metal

Finishing, 34, 41-52 (1957)

30. Polukarpov, M.N., Zhur. Obshchei Khim., 18, 1249-58 (1958)

31. Polukarpov, M.N., J. Gen. Chem., U.S.S.R., 19, a1-a28, (1949)

32. Samarcev, A.G., Trudy Gosudarst. Opt. Inst. Leningrad, 19, 16-25 (1933)

33. Samarcev, A.G., Z. Physik. Chem., A168, 45 (1934)

34. Schuldiner, Sigmund, and Hoare, James P., Can. J. Chem., 37, 228 (1959)

35. Stokes, R.A., and Robinson, R.H., "Electrolyte Solutions", 2nd Ed., Butterworth Scientific Publications, London, (1959), p. 414

36. Thompson, M.R., Trnas. Electrochem. Soc., 41, 351 (1922)

37. Tolansky, S., "Multiple Beam Interferometry," Oxford University Press (1948), p. 14-18.

APPENDIX I

APPLICATION OF THE SECOND WIEN EFFECT

Using the following expressions, presented by Harned and Owen[1] for the Second Wien effect:

$$\bar{b} = 2Bq = \frac{|z_1||w_1| + |z_2||w_2|}{|w_1| + |w_2|} \quad z_1 z_2 \frac{X \epsilon^2}{2D_k^2 T^2}$$

$$\frac{|z_1^2 z_2^2 (\lambda_1 + \lambda_2)}{|z_2| \lambda_1 + |z_1| \lambda_2} \quad 9.695 \frac{V}{DT^2}$$

which reduces in the case of a 2-2 electrolyte to

$$\bar{b} = 38.78 \frac{V}{DT^2}$$

and

$$\frac{\Delta\alpha}{\alpha_0} = \frac{(1-\alpha)}{(2-\alpha)} \bar{b} \quad ,$$

we may calculate the potential necessary for the dissociation of a detectable quantity of ion pairs.

By definition, α_0 is the degree of dissociation of the ions in the solution, or in other words, the fraction of the solute dissociated into ions. α_0 has been calculated (p. 105) to be about 45% or .45. The least detectable fringe shift would be about .05 or 1/20 fringe shift. As a complete dissociation of all undissociated ions would give a fringe shift of 3.042 fringes, which represents the dissociation of

---

[1] Harned, H.S., and Owen, B.B., "The Physical Chemistry of Electrolyte Solutions," Third Edition, The Reinhold Publishing Corp., New York, (1958) pp. 144-5

5.5 grams of solute in a solution containing 10 grams of solute (since in the bulk of the solution the other 4.5 grams are already dissociated).

$$\frac{x}{5.5} = \frac{.05}{3.042}$$

$x = .090$ grams of solute, dissociating as a result of the applied voltage. α thus changes from .45 to .459, giving $\Delta\alpha$ of .009. $\Delta\alpha/\alpha_0$ is thus about .02.

Taking $D = 78$, $T = 280^\circ K$, we obtain

$$.02 = \frac{1-.46}{2-.46} \quad 38.78 \quad \frac{V}{78\ (280)^2}$$

$V = 882$ volts/cm

The graph on p. 73 shows a sudden voltage increment of about .02 volts at about .65 millimeters electrode separation. This increment can agree with the theory above provided there is a sudden drop in voltage over a very short distance, that is, most of the available voltage in about 10^{-3} cm. It is possible that the acquiring of sufficient energy to cause dissociation and the actual dissociation might not occur simultaneously, that is, the ion-pair may diffuse some distance in the process of dissociating. Data to support or disprove this argument are not at present available to the author.

An experiment to ascertain whether this is the true

---

2. Berg, D., and Patterson, A., J.Am. Chem. Soc., 74, 4704 (1952)

B29790